A CONVENIENT METHOD FOR POTENTIOMETRIC TITRATION OF CHLORIDE IONS*

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The potentiometric titration of chloride ions as usually carried out is accurate but rather time-consuming and is not suitable for the determination of very small quantities.

The method described in the present paper can be used to determine small amounts of $10^{-4}$ molar, or stronger, chloride solutions with an accuracy of about ± 0.03 ml. $10^{-4}$ molar silver nitrate. The titration requires only a few minutes and a series of solutions may be titrated consecutively.

Solutions and Apparatus Required.—All reagents should be chloride-free if possible.

0.25 M potassium nitrate.
10$^{-4}$ M silver nitrate made up in 0.25 M potassium nitrate.
Calcium carbonate.
0.10 M sodium oxalate, 0.001 M silver nitrate, 0.1 M potassium nitrate (14 gm. sodium oxalate, 10 gm. potassium nitrate, and 10 ml. of 0.1 M silver nitrate in 1 liter).
2 silver electrodes.
Galvanometer: 0.5 × 10$^{-6}$ amperes per mm. or more sensitive.
2 ml. microburette graduated in 0.01 ml. (E. Machlett & Son, New York, No. A8-525).

Arrangement of Apparatus.—Preparation of Reference Electrode: A hole about 5 mm. in diameter is blown in the bottom of a 1 × 10 cm. pyrex test tube and the tube packed with glass wool and hyflo filter-cel (Johns-Manville Corporation) as shown in Fig. 1. The tube is filled with 0.1 M sodium oxalate, 0.001 M silver nitrate, 0.1 M potassium nitrate and some of the solution drawn through the filter-cel by suction. The tube is then filled completely with the solution

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The experiments referred to were first reported July 1, 1944.

The use of silver oxalate as a reference electrode was suggested by Dr. Edgar L. Eckfeldt of the Leeds and Northrup Company.
and the stopper and silver electrode forced in place. The stopper should be sealed or taped so as to prevent any air from leaking in.

Silver Electrodes: Silver foil about 1 X 5 X 0.1 cm. welded to No. 12 silver wire. Polish with fine emery paper and short circuit in 0.25 M potassium nitrate, 10^-4 M silver nitrate for 24 hours. The reference electrode should remain in good condition indefinitely but the titrating electrode may lose sensitivity so that equilibrium is reached too slowly. The sensitivity can be restored by polishing with emery cloth. This treatment causes the electrode to be negative for a few minutes and the first few titrations may be incorrect.

The titrating electrode should be bent in a cylinder and placed as low as possible in the funnel. It may be held in place by a rubber band on the reference cell.

Operating Directions.—Set up apparatus as in Fig. 1. Cover the silver electrode with 0.25 M potassium nitrate, calcium carbonate (about 10 ml.). Connect electrodes to galvanometer and put 2,000 to 3,000 ohms in parallel with galvanometer. The titrating electrode should be negative. Add about 1 ml.
$10^{-3}$ m silver nitrate. The titrating electrode should now be strongly positive. Add $10^{-3}$ molar chloride until the galvanometer reaches 0. There is usually a slight drift for a few minutes after which the galvanometer should remain constant. Chloride or silver ions are then added until the galvanometer remains constant at 0.

**Titration.**—Add 1 to 10 ml. of solution containing chloride ions to cell. Titrating electrode becomes negative. Run in silver nitrate until galvanometer returns to 0 and remains constant at 0 for at least 30 seconds. With sensitive electrodes the titration should require about 1 minute with $10^{-2}$ M or more concentrated silver nitrate, and 2 to 3 minutes with $10^{-1}$ M silver nitrate.

### TABLE I

<table>
<thead>
<tr>
<th>Cl taken—concentration, mols/liter</th>
<th>0</th>
<th>$10^{-4}$</th>
<th>$10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume of sample, ml.</td>
<td>0.5</td>
<td>1.0</td>
<td>0.25 0.5 1.0</td>
</tr>
<tr>
<td>Total volume in cell, ml.</td>
<td>8-10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver nitrate concentration, mols/liter</td>
<td>$10^{-4}$</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>Blank</td>
<td>0.08 0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver nitrate (corrected for blank), ml.</td>
<td>0.25 0.48 1.04</td>
<td>0.49 1.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.29 0.40 1.00</td>
<td>0.50 1.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.22 0.52 1.04</td>
<td>0.48 0.99</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.24 0.52 1.00</td>
<td>0.50 1.02</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>0.25 0.48 1.04</td>
<td>0.49 1.01</td>
<td></td>
</tr>
</tbody>
</table>

**Subsequent Titration.**—Do not empty cell but merely drain off solution until titrating electrode is just covered. This should not change galvanometer reading. If it does the galvanometer should be adjusted to 0 again before the next titration.

**Blank for Change in Volume.**—When titrating with $10^{-2}$ M silver a small titration is required when 1 ml. water is added. This blank titration is subtracted from the titration of the sample.

If $10^{-3}$ M or stronger silver nitrate is used a larger volume of solution may be kept in the cell. No blank titration is found with $10^{-3}$ M or stronger silver nitrate.

The results of some titrations of hydrochloric acid and various concentrations of silver nitrate are shown in Table I.

**SUMMARY**

A convenient reference cell and method of potentiometric determination of chloride ions with silver nitrate is described. The method is accurate to about ± 0.02 ml. $10^{-4}$ M silver nitrate.