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A VOLUMETRIC METHOD FOR CHLORIDE DETERMINATION USING AN ADSORPTION INDICATOR, WHICH IS APPLICABLE TO FIELD AND LABORATORY WORK[1]

by

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This volumetric method is referred to as "Fajans' Method", having been perfected by K. Fajans of the University of Michigan. We wish to acknowledge Professor Fajans' cooperation in helping to secure the essential data necessary for this paper.

The method described in this paper for chloride determination is based upon the fact that the dye is more strongly adsorbed on a silver chloride or silver bromide precipitate when a slight excess of silver nitrate is present. An excess of silver ions will provide the precipitate with a positive charge and the negative dyestuff ions will be adsorbed more strongly, giving a lilac colored precipitate. An excess of chloride or bromide ions will cause the precipitate to be negatively charged and the negative dyestuff ions will be less strongly adsorbed, giving a pink colored precipitate.

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[1] Contribution from the Institute for Fisheries Research of the Michigan Department of Conservation and from the Chemistry Department of the University of Michigan.

The color change of the precipitate from pink to blue therefore can serve as an indication of the equivalence point, i.e. the end point.

Cations of heavy metals such as lead and zinc and colored ions of iron and chromium may be present in the test sample during titration without interference.

Preparation of Reagents

1. N/10 silver nitrate solution. Place approximately 17.0 grams of analytical $AgNO_3$ in a beaker and dry for two hours at 110°C. and allow to cool. Weigh the beaker and silver nitrate, then transfer the $AgNO_3$ to another clean beaker or a one liter volumetric flask and dilute with distilled water up to one liter. Re-weigh the original beaker in order to determine the actual amount of $AgNO_3$ transferred. The normality of the $AgNO_3$ solution is calculated by using the following equation:

$$N = \frac{\text{Wt. of } AgNO_3 \text{ used in one liter of water}}{169.89 \text{ grams}}$$

This N/10 solution of $AgNO_3$ will be quite stable if kept in the dark. For checking the normality of the silver nitrate which has been prepared for some time, prepare a N/10 solution of sodium chloride by dissolving 5.846 grams of analytical sodium chloride in distilled water and diluting to one liter. Use a 40 ml. sample of this chloride solution for titration and follow the regular procedure outlined below. The 40 ml. of chloride sample should require 40 ml. of the N/10 $AgNO_3$, if not make a correction factor for the normality. As an example, suppose that in titration of a 40 ml. N/10 Na Cl sample it required 38.8 ml. of a silver nitrate solution to achieve the end point, then the normality of the $AgNO_3$ would be $0.100 \times \frac{40.0}{38.8} = 0.030$.

2. Phenosafranine indicator solution. Dissolve 0.2 grams of phenosafranine crystals in 100 ml. of distilled water.

Procedure

Place 40 ml. of the test solution into a 200 ml. flask and add from 8 to 10 drops of phenosafranine indicator, agitating the contents afterwards to thoroughly mix the dystuff. Titrate with N/10 $AgNO_3$ shaking the sample vigorously after each addition to complete as much as possible the coagulation of the precipitate which will appear as pink flakes. At intervals during titration, stopper the flask with a rubber stopper, shake, and invert to allow the precipitate to settle down in the neck where the color can easily be observed. Continue these operations until the color of the precipitate changes from a pink to lilac, indicating the end point.

For calculating the p.p.m. of chloride in the sample, use the following equation:

$$\frac{1,000}{\text{Vol. of sample}} \times \text{ml. of } AgNO_3 \text{ used in titration} \times N \text{ of the } AgNO_3 \times 35.46 = \text{p.p.m. of chloride}$$

Remarks

The writers have found that in testing various brine samples, the best results were obtained when using about 40 ml. of N/10 $AgNO_3$ for titration. Roughly this would represent a brine sample containing about 3,500 p.p.m. of chloride. It is suggested that when testing an unknown sample, a pilot sample be quickly run first in order to determine the approximate chloride content. If the amount of N/10 $AgNO_3$ used in titration falls within a range of 20 to 50 ml., then the general procedure can be followed. If, however, the amount of N/10 $AgNO_3$ does not fall within this range, alterations from the general procedure are desirable. Weak brine solutions containing less than 1,600 p.p.m. of chloride should be concentrated.

This can be accomplished by securing an adequate sample and boiling down to approximately 40 ml. The original volume is used in calculating the results. Likewise, a highly concentrated brine sample should be diluted with distilled water until it falls within the desired range. In computing the results, again the original volume is used.

This method has been used successfully by the Institute for Fisheries Research in brine analyses and has proven to be satisfactory for field and laboratory work. Since blank runs are not necessary, this method is quite rapid.

References

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