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THE DETERMINATION OF CHLORIDE IN THE PRESENCE OF PHOSPHATE

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# THE DETERMINATION OF CHLORIDE IN THE PRESENCE OF PHOSPHATE

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## ABSTRACT

The inconsistent results obtained in the estimation of chlorides in
an aqueous extract of ash from calcined samples of fish by means of the Mohr,
Volhard and gravimetric methods have been investigated.  The discrepancies are
attributed to the presence of phosphates.  By employing known solutions of
sodium chloride and phosphate it is shown that the Mohr method is useless and
the gravimetric method gives high values due to adsorption of phosphate.  The
Volhard method appears to be entirely satisfactory.

## INTRODUCTION

The quantitative estimation of chloride is one of the standard deter-
minations carried out when analysing fish products.  In performing this analysis
on aqueous extracts of ash from calcined fish samples, the Mohr method could not
be applied as no definite end point could be obtained during the titration with
silver nitrate using potassium chromate as indicator.

A satisfactory titration could be obtained with the Volhard method as
modified by Rothmund and Burgstaller (1909) but the results were low when com-
pared with those of the gravimetric determinations as shown in table I.  It
appeared necessary to investigate this analysis and determine which method would
give correct results.

## Table I. - Determination of chloride in fish ash

| Expt. | Percent Cl ion determined by: | |
| | Volhard method | gravimetric method |
| --- | --- | --- |
| 1. | 25.74 | 26.52 |
| 2. | 25.75 | 26.49 |

### EXPERIMENTAL

A solution of silver nitrate of concentration approximately 0.01 N was prepared and standardized against a standard solution of sodium chloride prepared from a recrystallized salt which had been dried at 110° C. The standardization of the silver nitrate solution was checked by gravimetric determination.

An approximately 0.01 N solution of potassium thiocyanate was prepared and standardized against the above silver nitrate solution using ferric alum as indicator.

A stock solution of sodium chloride containing 0.01534 gm. of chloride ion per milliliter was prepared from the purified sodium chloride described above.

A stock solution containing chloride and phosphate was prepared from the same pure medium chloride and recrystallized sodium dihydrogen phosphate, $NaH_2PO_4.H_2O$. The concentration of chlorine ion was 0.01334 gm. per millilitre, and that of the phosphate was 0.04105 gm. per millilitre.

ANALYSES OF PHOSPHATE-FREE CHLORIDE SOLUTION

The Volhard volumetric determination of chloride in the absence of phosphate was carried out in the following manner. Five ml. of the stock solution was pipetted into a 150-ml. beaker and acidified with 4 ml. of nitric acid (sp. gr. 1.32) to prevent the precipitation of silver phosphate. An accurately measured quantity (50 ml.) of the standard silver nitrate solution, corresponding to an excess over the amount equivalent to the chloride present, was added and the suspension boiled. After the precipitate was coagulated, the solution was filtered and the clear filtrate cooled before back-titrating with the standard potassium thiocyanate solution, using 2 ml. of ferric alum indicator. The results of these determinations are shown opposite experiments 3 and 4 in table II.

Table II. - Comparison of the Volhard and gravimetric determinations of chloride in phosphate-free solutions of sodium chloride. Actual concentration of chlorine ion = 0.01534 mg. per ml.

| Expt. | Concentration of Cl ion determined by: | |
| | Volhard method mg. per ml. | gravimetric method mg. per ml. |
|---|---|---|
| 3 | 0.01532 | 0.01533 |
| 4 | 0.01534 | 0.01536 |
| 5 | 0.01534 | 0.01534 |
| 6 | 0.01533 | 0.01535 |

Experiments 5 and 6, table II, show the results of determinations made in exactly the same manner except that the precipitated silver chloride was not filtered off before back-titrating with potassium thiocyanate. This was possible with the coagulated precipitate but not with the suspension, as in the latter case a reaction takes place which removes the coloured ferric thiocyanate, resulting in fading at the end point. This reaction may be represented by the

equation

$$3 \text{ AgCl} + \text{Fe(CNS)}_3 \longrightarrow 3 \text{ AgCNS} + \text{FeCl}_3.$$

This reaction is too slow to influence ordinary titrations when the precipitate is coagulated, thus the determination can be made without the extra step in the procedure required by filtering.

A blank was run for this titration to determine the amount of thiocyanate required to give the shade of red used as the end point. The blank value found was subtracted from the reading of the thiocyanate burette in order to determine accurately the amount of silver nitrate used in precipitating the chloride present in the sample.

The gravimetric analyses shown in table II for comparison were carried out in the standard manner. Ten ml. of the sample was pipetted into a beaker and after acidifying with 8 ml. of nitric acid an excess of silver nitrate solution was added. The suspension was boiled until coagulation was complete, then filtered through a Gooch crucible. The precipitate was washed with water containing a little nitric acid, then with cold water, and finally dried at 130°C. It was then cooled in a desiccator and weighed.

ANALYSES OF PHOSPHATE CONTAINING CHLORIDE SOLUTION

The analyses of chloride in the presence of phosphate were carried out in the same manner, and the results are given in table III.

In the Volhard volumetric analyses numbered 7 and 8 the silver chloride precipitate was filtered off before back-titrating with potassium thiocyanate. In analyses 9, 10, and 11 the coagulated silver chloride was allowed to remain in the solution.

Table III. – Comparison of the Volhard and gravimetric determinations
of chloride in solutions containing sodium chloride and
sodium dihydrogen phosphate. Actual concentration of
chlorine ion = 0.01534 mg. per ml.

| | | Concentration of Cl ion determined by: | |
|---|---|---|---|
| Expt. | Volhard method mg. per ml. | gravimetric method (single precipitation) mg. per ml. | gravimetric method (double precipitation) mg. per ml. |
| 7 | 0.01538 | 0.01588 | 0.01544 |
| 8 | 0.01534 | 0.01580 | 0.01548 |
| 9 | 0.01536 | 0.01592 | - |
| 10 | 0.01534 | 0.01591 | - |
| 11 | 0.01538 | - | - |
| Mean | 0.01536 | 0.01588 | 0.01546 |

In addition to the gravimetric method described in the last section, a
modification involving double precipitation was employed to reduce the amount
of adsorption of phosphate on the silver chloride precipitate. After the
precipitation and coagulation in the usual way, the precipitate was filtered
and washed, then dissolved in concentrated ammonium hydroxide solution. The
silver chloride was reprecipitated by acidifying the solution with nitric acid
and adding a few millilitres of silver nitrate solution followed by boiling,
filtering, washing, drying and weighing as before. The results obtained by
this modification are presented in the last column of table III.

In order to prove that phosphate was adsorbed on the surface of the
silver chloride precipitate, a sample of the precipitate was taken, dissolved
in concentrated ammonium hydroxide, and treated with a solution containing
magnesium and ammonium nitrates. In a short time a slight crystalline pre-
cipitate of magnesium ammonium phosphate settled out. This was filtered off
on a small filter, dissolved in a drop of dilute hydrochloric acid, and the
ammonium molybdate test applied. A characteristic yellow precipitate was
obtained after warming and allowing to stand, thus confirming the test for

phosphate.

<div align="center">DISCUSSION.</div>

## MOHR METHOD

When the chloride in a sample containing phosphate is titrated directly with standard silver nitrate using potassium chromate indicator, the phosphate interferes with the sudden formation of the coloured silver chromate at the end point. Since the yellow silver phosphate is less soluble than the red-orange silver chromate, it is formed first as the end point is approached and the colour observed shades from yellow into orange-red, making it impossible to decide on a definite termination of the titration. The values are too high due to the precipitation of some phosphate before the first indication of the colour of the silver chromate can be observed. This method is obviously un-suited for the analysis of chloride in fish ash.

## VOLHARD METHOD

When phosphate was absent the Volhard method gave results that agreed closely with those of the gravimetric determination as seen in table II, but the results in table III show that this was not so when phosphate was present in the solution. However, the mean value of the results obtained by the Volhard method was only 0.13% higher than the theoretical value.

## GRAVIMETRIC METHOD

From table III, the mean value of the results obtained by the gravimetric analysis employing one precipitation only is 3.52% too high, presumably due to the adsorption of phosphate on the surface of the precipitated silver chloride. When the precipitate was dissolved in strong ammonium hydroxide and reprecipi-tated by the action of nitric acid the mean value of the results was 0.78% too

high, indicating that some adsorption had been eliminated. The labour of re-precipitating does not warrant the increase in accuracy in view of the much more accurate results by the Volhard method.

REMOVAL OF PHOSPHATE PRELIMINARY TO MOHR TITRATION

The removal of phosphate by precipitation with calcium or barium nitrate preliminary to titration by silver nitrate requires the solution to be filtered as an additional operation. The precipitation of the phosphates requires an alkaline solution while the titration according to the Mohr method requires a neutral solution. This procedure entails too much care and too many operations for the method to be practical for rapid determinations.

CONCLUSION

The Volhard method is the most satisfactory method for the determination of chloride in the presence of phosphate as found in fish ash.

ACKNOWLEDGEMENTS

REFERENCES.

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