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**THE POTENTIOMETRIC TITRATION
OF CHLORIDES**

by

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MINERAL SCIENCES DIVISION

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Leonard G. Ripley* and W. R. Inman**

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SUMMARY OF RESULTS

Chlorides can be potentiometrically titrated with silver nitrate using a Ag//Ag/Cl electrode system. The end-point is determined graphically. This method has been quantitatively employed to determine chlorides in many chloride salts. The useful range, without any modification, is 2 mg and up. However, it has been found that through the addition of known quantities of potassium chloride and by cooling the sample solutions to less than 10°C, before titrating, the limit can be extended downward. Further, the limit can be extended to 50 micrograms, through the steam distillation isolation procedure when trace amounts of soluble chlorides are collected from larger sample weights (5-25 g) prior to being "spiked" with potassium chloride and cooled to less than 10°C before titrating.

The purpose of this report is to describe some of the variables affecting the potentiometric titration of chlorides.

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INTRODUCTION

The argentometric titration is one modification of the volumetric approach to the chloride ion determination. The technique of following the progress of a silver nitrate titration of chloride ion by measuring the potential between a silver and a silver halide electrode system has been known for nearly seventy years (1).

The potentiometric titration of the chloride ion has not been applied generally because the break in the potential at the end-point is not pronounced (2).

This report describes the condition under which this titration has been successful.

APPARATUS

Leeds and Northrup pH indicator, AC mains operated, Model No. 7664 with a pure silver electrode No. 1261 (Beckman, Billet style) and a silver-silver chloride reference electrode No. 1199-72 (Leeds and Northrup).

Magnetic stirrer (Magne-stir).

Graph paper (Hughes Owens No. 315F).

REAGENTS

Baker's analyzed reagent potassium chloride:

Certified to assay 99.7% KCl, which was dried at 110°C for 1 hr before using. This reagent was used in one of three ways:

- (a) Direct weights of 0.1000 - 0.4000 g dissolved in acids as required.
- (b) Stock solution (A) - 1 g of potassium chloride was dissolved in distilled water and diluted to 1 litre. Suitable aliquots were used, (1 ml is equivalent to 0.0004756 g Cl).
- (c) Stock solution (B) - 100 ml of stock solution (A) was diluted to 1 litre. Suitable aliquots were used, (1 ml is equivalent to 0.000047 g Cl).

Silver nitrate titrating solutions:

Merck's reagent grade silver nitrate was dissolved in distilled water. Three working solutions were used:

- (a) 0.25 N AgNO₃ - 42.5 g of silver nitrate were dissolved in distilled water and diluted to 1 litre, (1 ml is equivalent to 0.0090 g chloride ion).

- (b) 0.05 N AgNO_3 - 8.5 g of silver nitrate were dissolved in distilled water and diluted to 1 litre, (1 ml is equivalent to 0.0018 g chloride ion).
- (c) 0.01 N AgNO_3 - 200 ml of 0.05 N AgNO_3 solution were diluted to 1 litre, (1 ml is equivalent to 0.00036 g chloride ion).

The silver nitrate titrating solutions were standardized against potassium chloride solutions which contained a chloride ion concentration in the same range and under similar acid conditions as existed in the sample solutions.

TECHNIQUE

The progress of the titration was followed by plotting the potential produced after each addition of the silver nitrate. These additions were varied from 1.0 to 0.10 ml, the smallest volume being used in the region of the end-point. The actual end-point was then determined by calculating the point of inflection obtained by projecting the lines as in Figure 1. The mid-point 'C' of the line 'AB' is the point of inflection and also the end-point.

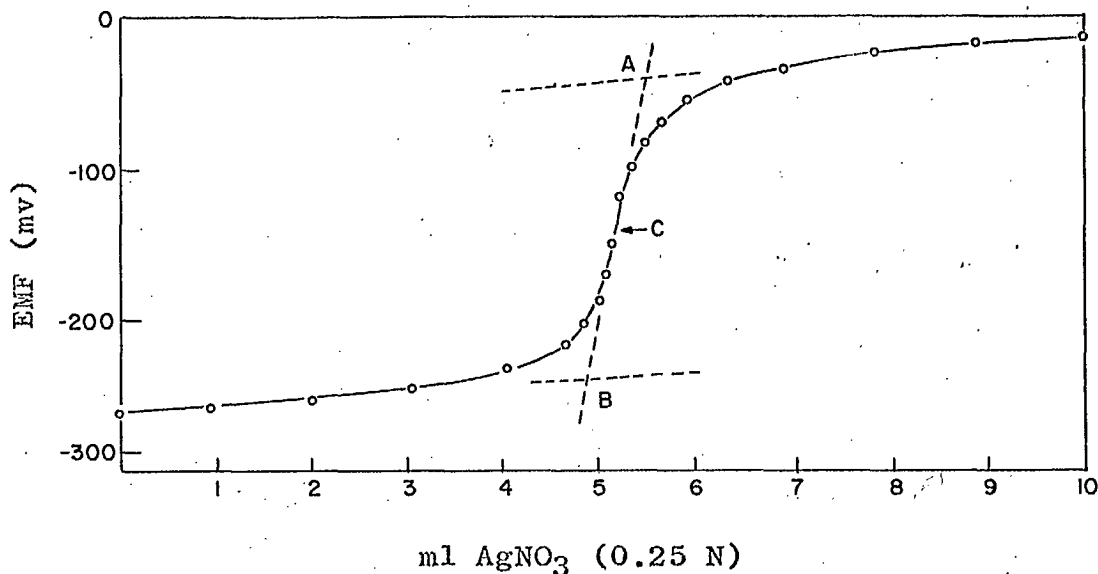


Figure 1 - Typical Chloride Titration Curve

RESULTS AND DISCUSSION

Experiments have shown that the height and the form of the wave pattern were dependent on several variables.

(a) Effect of the Acid Medium

Sulphuric acid with nitric acid has been found to be a suitable medium. The effect of varying the sulphuric acid medium from nil to 10% is shown in Figure 2.

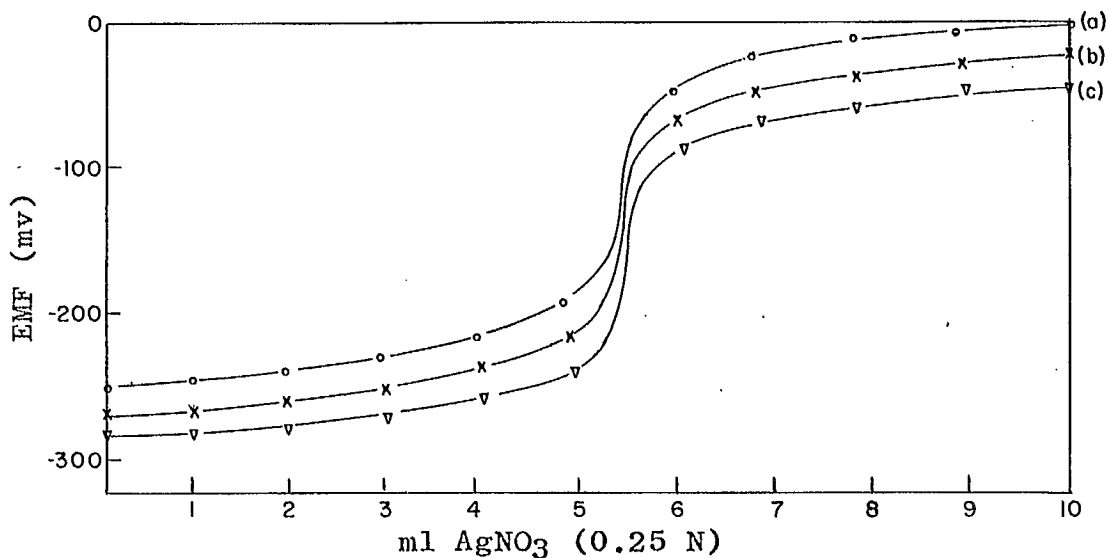


Figure 2 - Effect of Sulphuric Acid

These titrations were performed under the following conditions:

Curve (a) - 0.1000 g of KCl was dissolved in 300 ml of distilled water and 5 ml concd nitric acid added. Titration was made at room temperature with 0.25 N silver nitrate.

Curve (b) - 0.1000 g of KCl was dissolved in 300 ml of 5% sulphuric acid and 5 ml concd nitric acid added. Titration was made at room temperature with 0.25 N silver nitrate.

Curve (c) - 0.1000 g of KCl was dissolved in 300 ml of 10% sulphuric acid and 5 ml concd nitric acid

added. Titration was made at room temperature with 0.25 N silver nitrate.

Although the potential of the end-point decreased with increasing acidity, the net wave height and shape were unaffected.

When the amount of concentrated nitric acid added to 300 ml of 5% sulphuric acid medium containing 0.1000 g KCl, was varied from nil to 10 ml, the titration wave patterns resembled the effect of increasing the sulphuric acid (Figure 2). However, the increase in the potential of the end-point was much smaller.

(b) Effect of Volume of Solution

The titration curves, shown in Figure 3, resulted from three solutions, containing 10 mg of potassium chloride, which were diluted with various amounts of 5% sulphuric acid.

The three curves in Figure 3 indicate the following dilutions:

- (a) 100 ml of 5% sulphuric acid with 5 ml concd nitric acid.
- (b) 300 ml of 5% sulphuric acid with 5 ml concd nitric acid.
- (c) 500 ml of 5% sulphuric acid with 5 ml concd nitric acid.

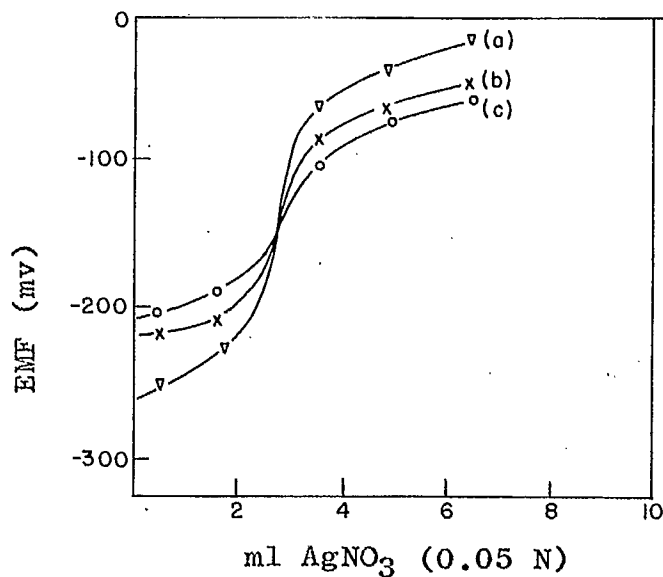


Figure 3 - Effect of Dilution on the Titration Curve

The wave height is affected by dilution, and the best wave would be obtained when titrations are made on the most concentrated solution feasible.

(c) Effect of the Strength of Silver Nitrate
Titrating Solution

Good titration curves are obtained with the 0.25 N silver nitrate titrant as shown in Figure 4.

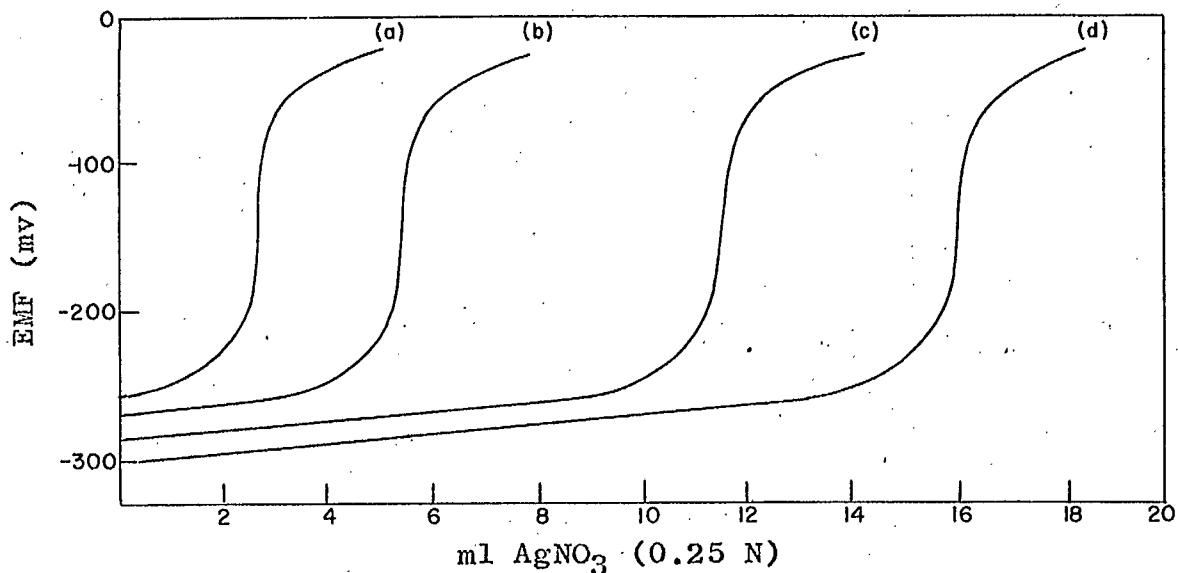


Figure 4 - Titration Curves with 0.25 N AgNO_3 .

These four curves are based on an acid medium of 300 ml of 5% sulphuric acid and 5 ml concentrated nitric acid containing the following amounts of potassium chloride:

- (a) - 50 mg
- (b) - 100 mg
- (c) - 200 mg
- (d) - 300 mg

The titration curves show less verticality when a weaker titrating solution (0.05 N AgNO_3) is used. This effect is shown in Figure 5.

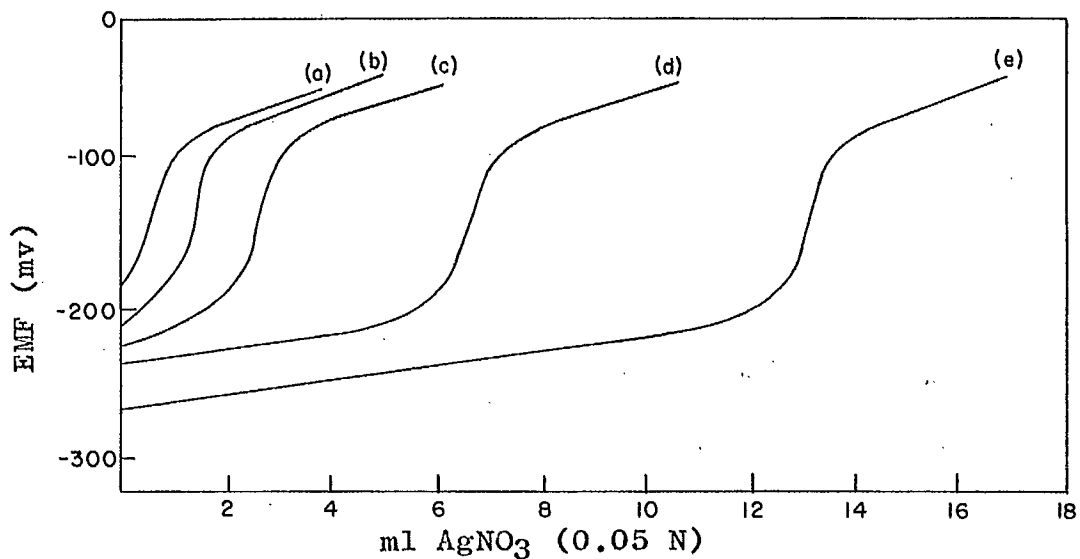


Figure 5 - Titration Curves with 0.05 N AgNO_3

These five curves are based on an acid medium of 300 ml of 5% sulphuric acid and 5 ml concentrated nitric acid containing the following amounts of potassium chloride:

- (a) - 1 mg
- (b) - 5 mg
- (c) - 10 mg
- (d) - 25 mg
- (e) - 50 mg

The slope of the titration curve is less pronounced when 0.01 N AgNO_3 is the titrant, as shown in Figure 6.

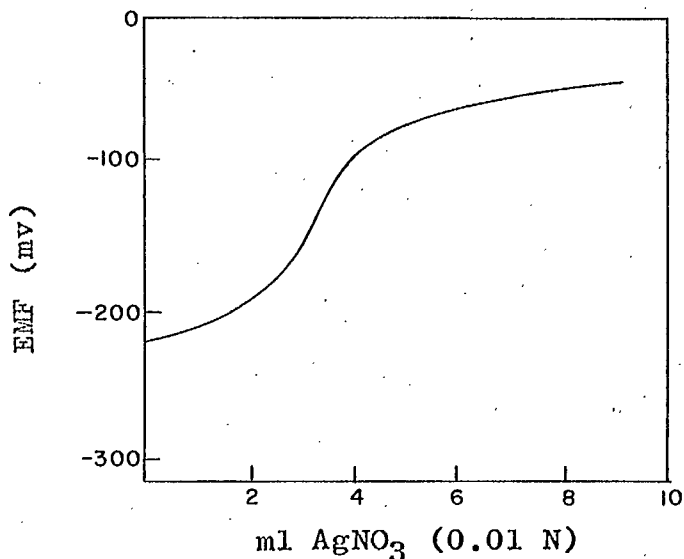


Figure 6 - Titration Curve with 0.01 N AgNO₃

This curve is based on an acid medium of 100 ml of 5% sulphuric acid and 5 ml concentrated nitric acid containing 2.5 mg of potassium chloride.

It is apparent that the lower chloride ion concentrations, which required a weaker silver nitrate titrating solution, resulted in a less abrupt curve, and for very low chloride ion concentrations (less than 2 mg) the end-point becomes difficult to distinguish.

This difficulty is overcome readily by the addition of specific aliquots of standard potassium chloride solutions (either stock solution (A) or (B)) to the sample solution before titrating. The actual titration for the sample is obtained by difference, the titre for the potassium chloride addition being obtained on another

aliquot. This technique gives an accurate method for determining small amounts of chloride ion.

(d) Effect of Temperature

The wave patterns are accentuated by chilling the solutions before titrating. The effect of temperature is most noticeable at lower chloride ion concentrations used, and provides a convenient means for improving the wave pattern when titrating small amounts of chloride ion. These sample solutions are therefore cooled in an ice bath to less than 10°C prior to titration.

The effect of temperature is shown in Figure 7.

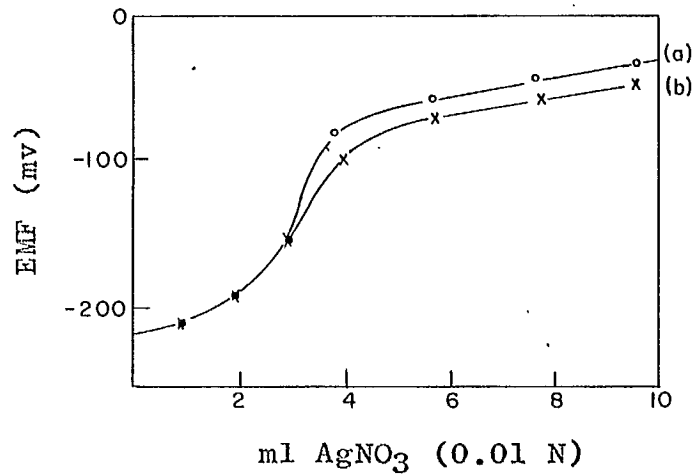


Figure 7 - Effect of Temperature on Titrations

These solutions each containing 2.5 mg of potassium chloride in 100 ml of 5% sulphuric acid and 5 ml concentrated nitric acid were titrated with 0.01 N

AgNO₃ at two different temperatures:

- (a) at less than 10°C
- (b) at room temperature (approximately 25°C)

The temperature effect can also be used to advantage when solutions of large volume are titrated, as shown in Figure 8.

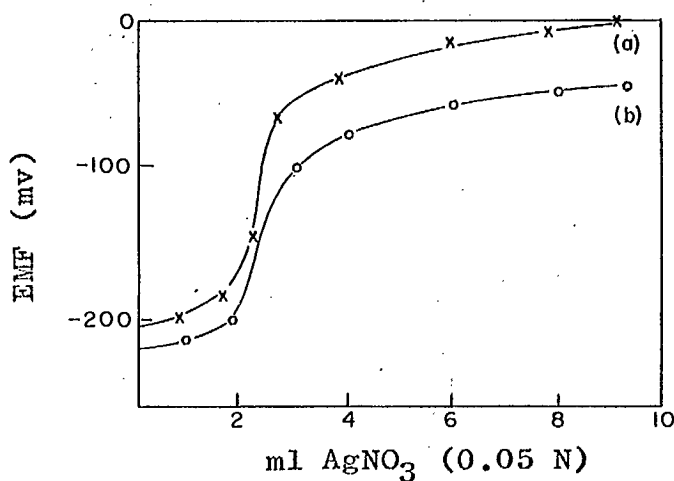


Figure 8 - Effect of Temperature on Large Volume Titrations

In this case, two samples of solutions containing 10 ml of potassium chloride stock solution A (10 mg KCl) in 500 ml of 5% sulphuric acid and 5 ml concentrated nitric acid were titrated with 0.05 N AgNO₃ at two different temperatures.

- (a) at less than 10°C
- (b) at room temperature (approximately 25°C)

It is apparent from the data summarized above that the wave pattern is dependent on several parameters which can be controlled at the time of titration.

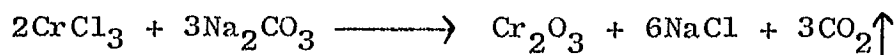
SAMPLE PREPARATION

(a) Soluble Chloride Salts

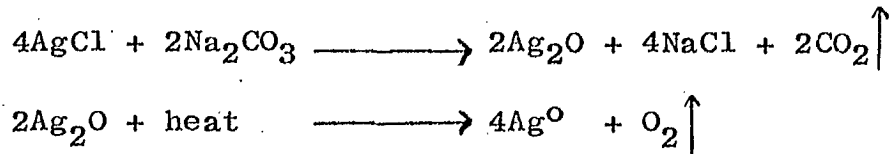
Sample weights of 0.2 to 1 g were dissolved directly in 5% sulphuric acid and 5 ml of concentrated nitric acid added. The solution is then ready for titration. Samples of this type which have been analyzed are: CeCl₃, FeCl₂, KCl, K₂TiCl₆, MgCl₂, MnCl₂, NaCl, SnCl₂, TiCl₂, TiCl₃, ThCl₄ and UCl₄.

(b) Insoluble Chloride Salts

Four acid-insoluble chloride salts, which have been encountered, were fused with anhydrous sodium carbonate. Sample weights of 0.2 to 1 g were fused with 10 g of sodium carbonate in a nickel crucible. In the case of CrCl₃, the fusion reaction was:



In the case of AgCl, CuCl and TiCl, the reaction is similar except the oxides produced are decomposed to free metal, as shown in the case of AgCl:



In both cases, the melt was leached with water and the insoluble material filtered off. The filtrate was made acidic with sulphuric acid until a 5% acid medium was obtained, and then 5 ml of concentrated nitric acid was added. The solutions were titrated as described previously.

(c) Trace Amounts of Soluble Chloride Salts

A third group of samples encountered were those that contain small amounts of acid soluble chlorides in a mixture of foreign salts. The easiest separation of the chloride ion is via steam distillation (3). The apparatus is shown in Figure 9.

The procedure followed in using the apparatus is as described in the following outline.

Sample weights up to 25 g are placed in the reaction flask. The apparatus is assembled and when a receiver containing 100 ml of 2% sodium hydroxide solution is in position, 20 ml of water and 50 ml of concentrated sulphuric acid are added through the funnel.

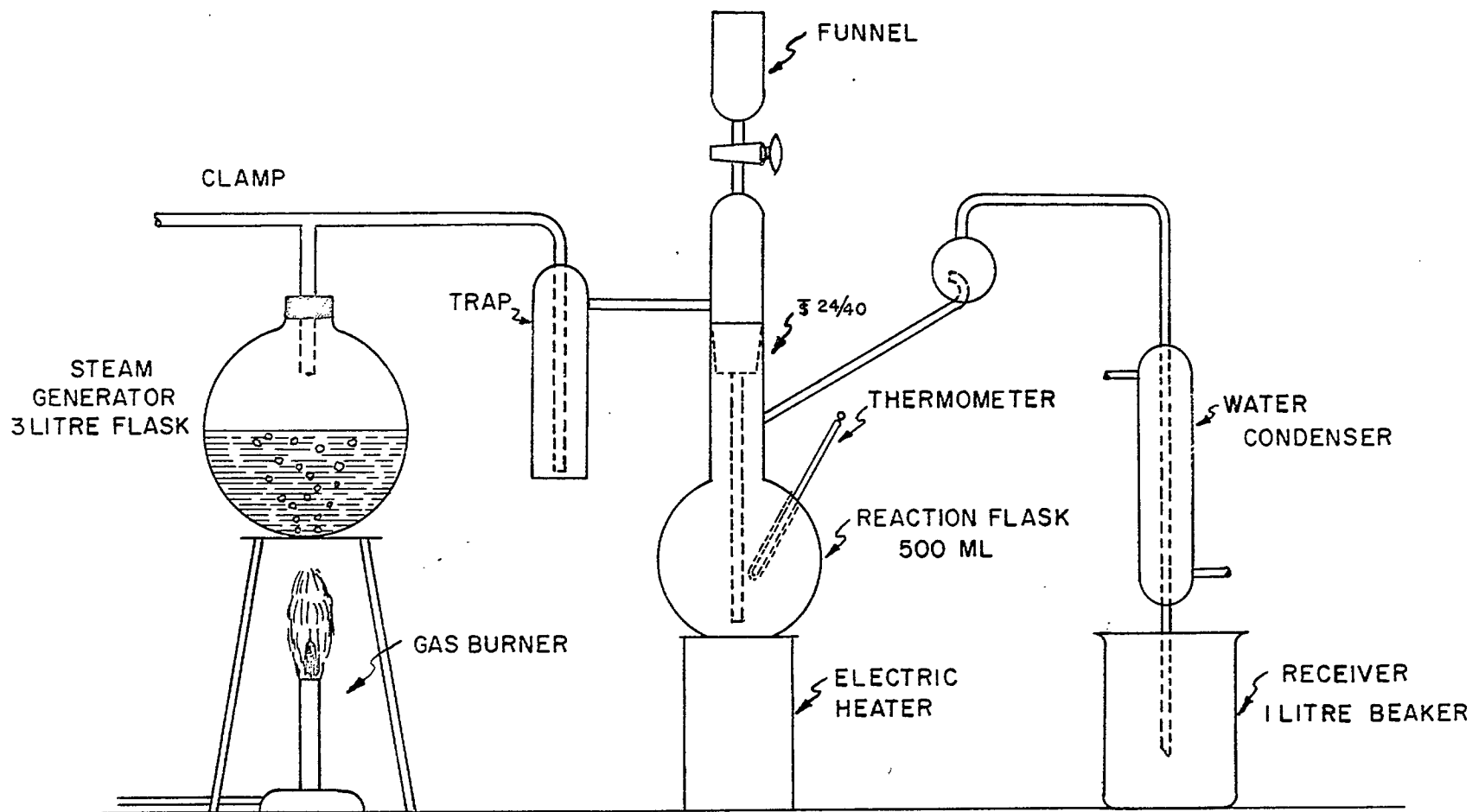


Figure 9 - Steam Distillation Apparatus

The heater is turned on and when the temperature in the reaction flask reaches 135°C, the steam is admitted to the reaction flask and the hydrogen chloride, which is produced, is distilled at a reaction flask temperature of 150°C until 400 to 500 ml of distillate is obtained.

The receiver is removed and cooled. The solution is neutralized, then made 5% acidic with respect to sulphuric acid, and 5 ml concentrated nitric acid added. The solution is then ready for titrating. However, in the case of low chloride ion concentrations, the solution is cooled to less than 10°C then titrated. Also, for very low chloride ion concentrations, the filtrate is "spiked" with an aliquot of a potassium chloride solution before cooling and titrating.

A reagent blank solution is prepared by the above procedure and is treated under the same conditions as the samples.

This procedure has a lower limit in the order of 50 micrograms of chloride ion.

CONCLUSIONS

The plotting on graph paper of the comparison of standard (known) solution with unknown samples, which have been treated identically, eliminates the errors that would have been caused by the acid medium, solution

volume, strength of reagents, and temperature.

Through the utilization of steam distillation of hydrogen chloride from large sample weights, "spiking", and temperature control, prior to potentiometric titration, the chloride ion can be determined to a lower limit in the order of 50 micrograms.

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