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SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDES

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MINERAL SCIENCES DIVISION

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SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDES

by

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

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SUMMARY OF RESULTS

The variables in the mercuric thiocyanate-ferric perchlorate spectrophotometric procedure for the determination of chlorides have been studied in some detail. An inherent background effect is described. A steam distillation isolation of hydrogen chloride has been found to be a suitable sample preparation procedure prior to the spectrophotometric determination.

This spectrophotometric procedure is useful for chloride determinations in the range of zero to 600 micrograms.

Results obtained on three zinc oxide samples are given.

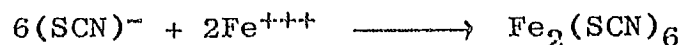
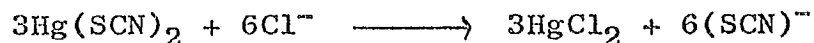
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INTRODUCTION

Chlorides can be determined spectrophotometrically by a method based on the following equations:



The red colored ferric thiocyanate complex, which is indicative of the chloride content, has a minimum transmittancy at 460 m μ .

This method, according to Zall et al (1), was first proposed by Utsumi (2) in 1952 and followed up by Iwasaki (3) the same year.

Zall describes an application of this method for the determination of chlorides in water, with a procedure that used a saturated aqueous solution of mercuric thiocyanate.

Henicksman et al (4) applied this method in 1959, to the determination of chlorides produced from the combustion of organic chlorine compounds. In the procedure it was recommended that a saturated alcoholic mercuric thiocyanate be used.

The purpose of the present paper is to report the conclusions obtained after several of the variables of this colorimetric procedure were examined.

APPARATUS

Beckman B Spectrophotometer with 1 cm and 5 cm cuvettes.

REAGENTS

Baker's Analyzed Reagent Potassium Chloride (certified to assay 99.7% KCl):

This reagent was dried at 110°C for 1 hour before using. A stock solution was prepared by dissolving 1 g potassium chloride in 1 litre of distilled water and then a 20 ml aliquot of this solution was diluted to 500 ml. (1 ml is equivalent to 0.000019 g chloride ion).

Mercuric Thiocyanate (aqueous):

A saturated aqueous solution (0.07%) was prepared by dissolving 1.000 g mercuric thiocyanate (Fisher's certified reagent) in a litre of distilled water. This solution was heated to near boiling for 1 hour, then cooled over night at room temperature, and filtered to remove the excess mercuric thiocyanate.

Mercuric Thiocyanate (alcoholic):

A saturated alcoholic solution was prepared by dissolving 1.000 g mercuric thiocyanate in a litre of 96% ethanol. This solution was heated to near boiling, then cooled over night at room temperature, and filtered to remove the excess mercuric thiocyanate.

Ferric Perchlorate:

This solution was prepared by dissolving 14 g of pure iron (N.B.S. No. 55d) in 1:1 nitric acid, then 120 ml of perchloric acid (70-72%) was added and the solution taken to fumes. After cooling, the solution was diluted to 1 litre with distilled water.

Perchloric Acid:

Nichols Chemical Co., (70-72%) reagent grade.

RESULTS AND DISCUSSION

Standard Curve

The procedure as specified by Zall was followed in the preparation of a standard curve for the range of 100-600 micrograms of chloride ion. Aliquots of potassium chloride stock solution were placed in 100 ml volumetric flasks with the following reagents:

10 ml HClO_4

2 ml $\text{Hg}(\text{SCN})_2$ (aqueous solution)

4 ml $\text{Fe}(\text{ClO}_4)_3$

and made up to volume with distilled water. The resulting color intensity curves are shown in Figure 1.

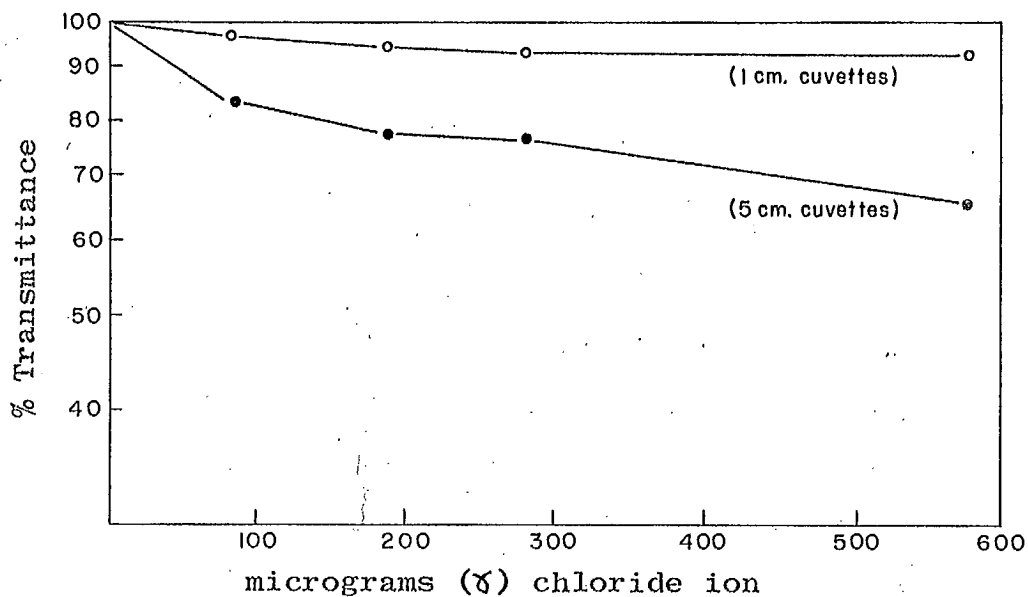


Figure 1 - Color Intensity Curve, using Zall's Procedure

Both of these curves are too flat and erratic to be suitable for routine work.

An investigation of the controlling parameters was undertaken in an effort to find a suitable colorimetric procedure for the range of 100 to 600 micrograms of chloride ion. In order to study the effect of concentration changes of the various reagents on the color intensity, a series of six standard curves was prepared based on 100 to 600 micrograms of chloride ion in 100 ml volumetric flasks.

The quantities of the reagents used in each were as follows:

- a) 10 ml HClO_4
2 ml $\text{Hg}(\text{SCN})_2$ (aqueous solution)
4 ml $\text{Fe}(\text{ClO}_4)_3$
- b) 10 ml HClO_4
10 ml $\text{Hg}(\text{SCN})_2$ (aqueous solution)
4 ml $\text{Fe}(\text{ClO}_4)_3$
- c) 10 ml HClO_4
10 ml $\text{Hg}(\text{SCN})_2$ (aqueous solution)
10 ml $\text{Fe}(\text{ClO}_4)_3$
- d) 2 ml HClO_4
10 ml $\text{Hg}(\text{SCN})_2$ (aqueous solution)
10 ml $\text{Fe}(\text{ClO}_4)_3$
- e) 10 ml HClO_4
20 ml $\text{Hg}(\text{SCN})_2$ (aqueous solution)
10 ml $\text{Fe}(\text{ClO}_4)_3$
- f) 10 ml HClO_4
10 ml $\text{Hg}(\text{SCN})_2$ (aqueous solution)
20 ml $\text{Fe}(\text{ClO}_4)_3$

The resulting color intensities were determined spectrophotometrically in 5 cm cuvettes at 460 $\text{m}\mu$. The results are shown in Figure 2.

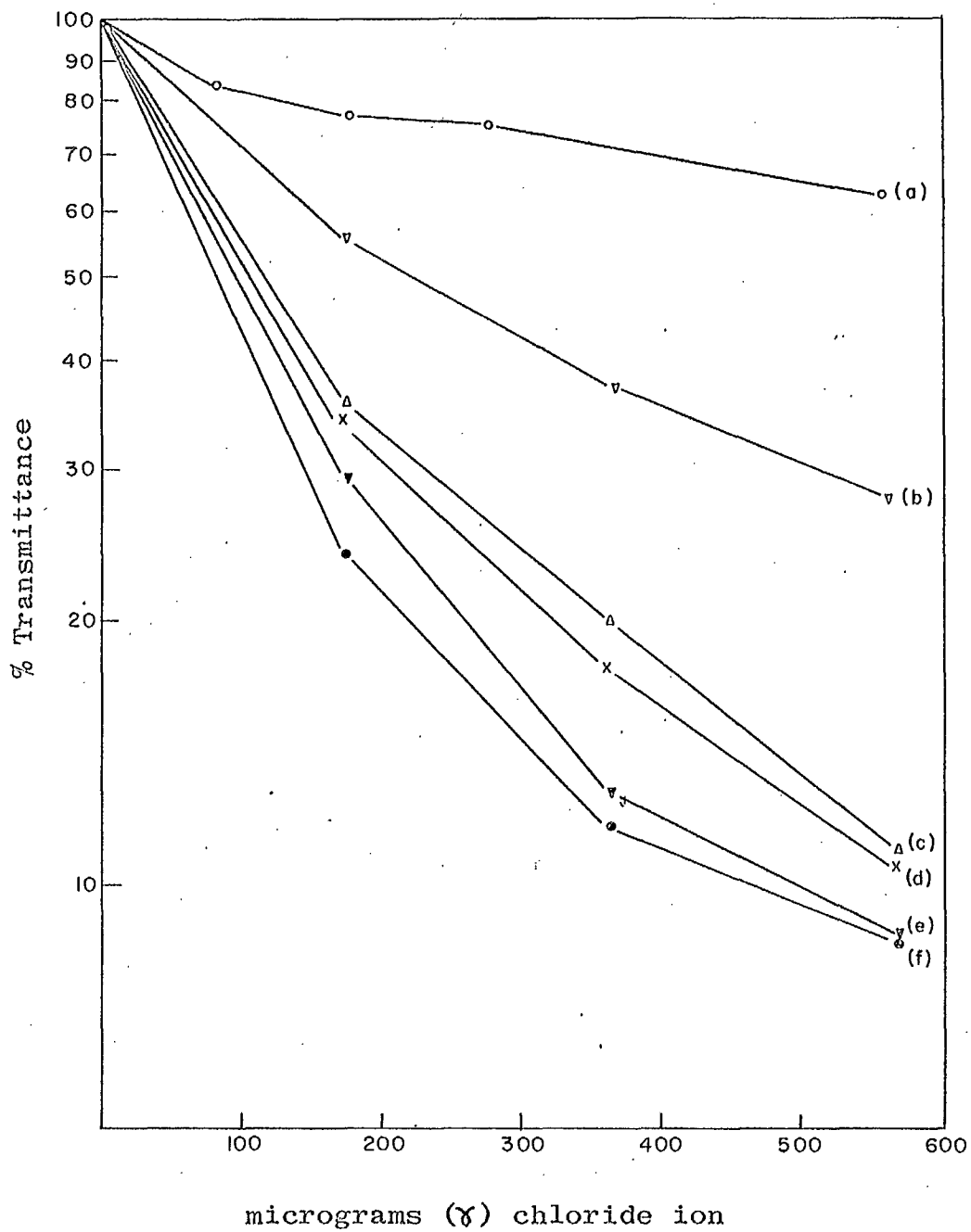


Figure 2 - Effect of Varying the Amounts of Reactants Used

The following conclusions can be drawn from Figure 2:

1. If the aqueous mercuric thiocyanate concentration is increased from 2 ml as in (a) to 10 ml as in (b), the color intensity is increased.

2. If the perchloric acid is increased from 2 ml as in (d) to 10 ml as in (c), the color intensity is decreased slightly.

3. If the ferric perchlorate is increased from 4 ml as in (b) to 10 ml as in (c) and to 20 ml as in (f), the color intensity is increased. Therefore, a more sensitive curve can be obtained by increasing the mercuric thiocyanate and/or ferric perchlorate concentrations.

Three relevant variables were also considered:

1. An alcoholic solution of mercuric thiocyanate was substituted for the aqueous mercuric thiocyanate solution to determine if the color intensity could be further increased. When a 10 ml aliquot of the alcoholic solution was used, some mercuric thiocyanate was precipitated out causing turbidity. If smaller aliquots of alcoholic mercuric thiocyanate were used, a point was reached at about 2 ml where turbidity did not occur. It has been found that the color intensity of a 100 ml solution containing 2 ml alcoholic mercuric thiocyanate

is approximately equal to one containing a 10 ml aliquot of aqueous mercuric thiocyanate; therefore, no advantage is evident through the use of an alcoholic mercuric thiocyanate solution.

2. There was no evidence that the temperature of the solution at the time of mixing the reactants was critical.

3. The relative stability of the color intensity of solutions (used in Figure 2) was observed when these solutions were allowed to stand for 18-24 hours. The general trends were:

- a) Very little fading occurred when the concentration of mercuric thiocyanate was increased.
- b) The rate of fading appeared to be proportional to the ferric perchlorate concentration.
- c) The color intensity was enhanced at the lower perchloric acid concentration.

The best condition for stability of colour, and also to provide a suitable working standard curve for the range of 100 to 600 micrograms of chloride ion, was curve (c) in Figure 2, ie

10 ml HClO_4

10 ml $\text{Hg}(\text{SCN})_2$ (aqueous solution)

10 ml $\text{Fe}(\text{ClO}_4)_3$

made up in 100 ml volumetric flasks with distilled water.

The fading of the color under these conditions is shown in Table 1.

TABLE 1

Fading with Respect to Time

λ Cl	% Transmittance	
	Standing 20 minutes	Standing 24 hours
190	36.8	37.5
380	19.8	21.0
570	11.0	11.8

In practice, the solutions are read on the spectrophotometer within 10 to 20 minutes after developing the color.

Background Chloride Effect

It is observed, also, from Figure 2, that the color intensity is not directly proportional to the chloride ion concentration. This may be caused by an association of the absorbing molecules or ions taking place at the higher concentrations. Because of this characteristic the standard curves are dependent on the background chloride as well as on the difference in chloride level between the blank and the sample solutions. The effect of background chloride is shown in Figure 3.

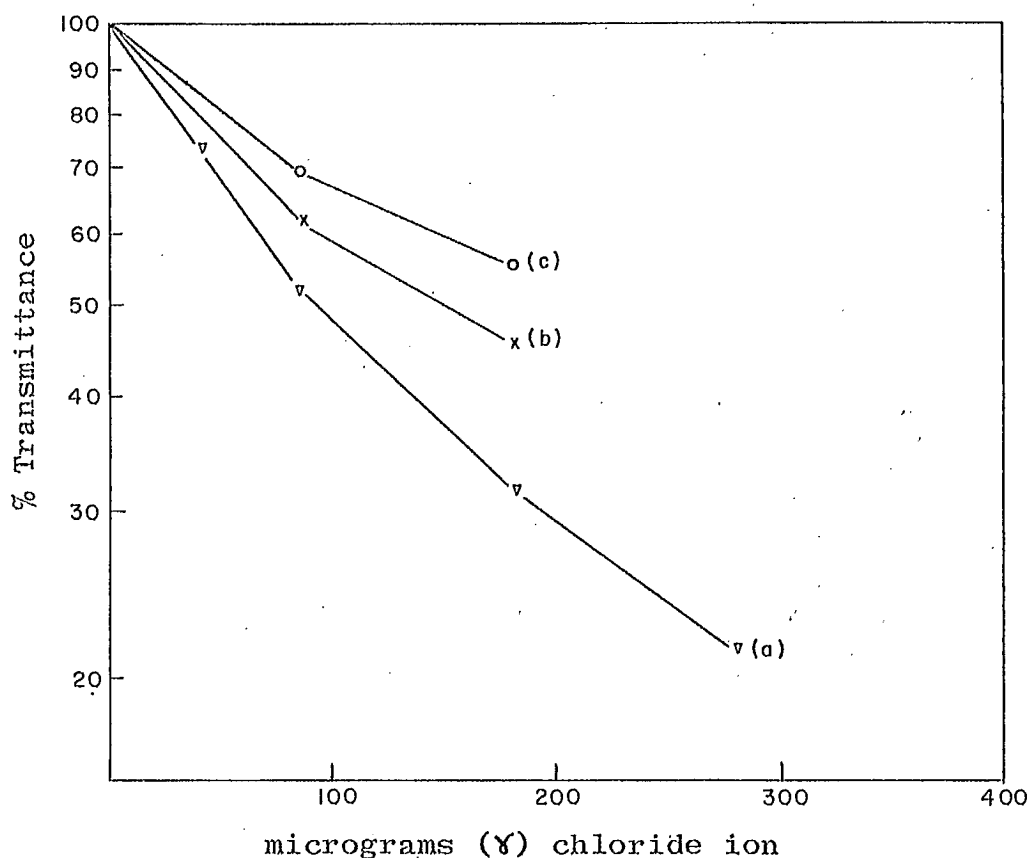


Figure 3 - Effect of Background Chloride

These three standard curves were prepared as follows:

- a) Chloride ions were added to 25 ml aliquots of a distilled* solution which contains 5γ chloride ions.
- b) Chloride ions were added to 25 ml aliquots of a distilled* solution which was known to contain 119γ of chloride ion per aliquot.
- c) Chloride ions were added to 25 ml aliquots of a distilled* solution which was known to contain 238γ of chloride ion per aliquot.

*These distilled solutions were obtained from the procedure described on page 14.

Also, the background chloride effect was observed when standard curves were prepared by adding chloride ions to aliquots of the reagent blank from different fusions, as shown in Figure 4. (A curve based on distilled water is shown for comparison).

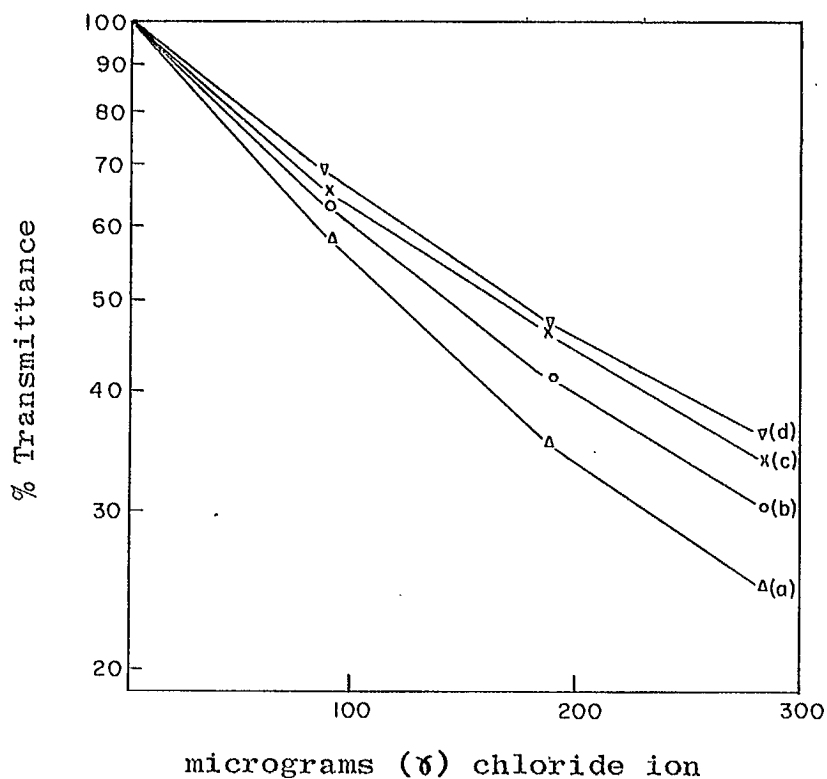


Figure 4 - Effect of Background Chloride from Fusion Mixtures

The background solutions were as follows:

- a) Distilled water.
- b) Aliquots of a solution resulting from a sodium carbonate fusion - each aliquot contained 1.0 g of sodium carbonate.

- c) Aliquots of a solution resulting from a sodium carbonate plus sodium nitrate fusion - each aliquot contained 1.0 g sodium carbonate and 0.2 g sodium nitrate.
- d) Aliquots of a solution resulting from a sodium carbonate plus potassium nitrate fusion - each aliquot contained 1.0 g sodium carbonate and 0.2 g potassium nitrate.

The background chloride arises from the presence of chlorides in the reagents.

Significant background chloride was also present when soluble chlorides were leached out with a caustic solution.

The error that would be caused by the background effect becomes minimal when the standard curve is prepared under the same conditions as the samples. The technique used was to take aliquots of the reagent blank as the basis for the standard curve, then all solutions should contain the same background chloride.

Steam Distillation

An alternative sample preparation technique involved a sulphuric acid attack of the sample in a closed glass system and the steam distillation of the soluble chlorides as hydrogen chloride (5). The apparatus is shown in Figure 5.

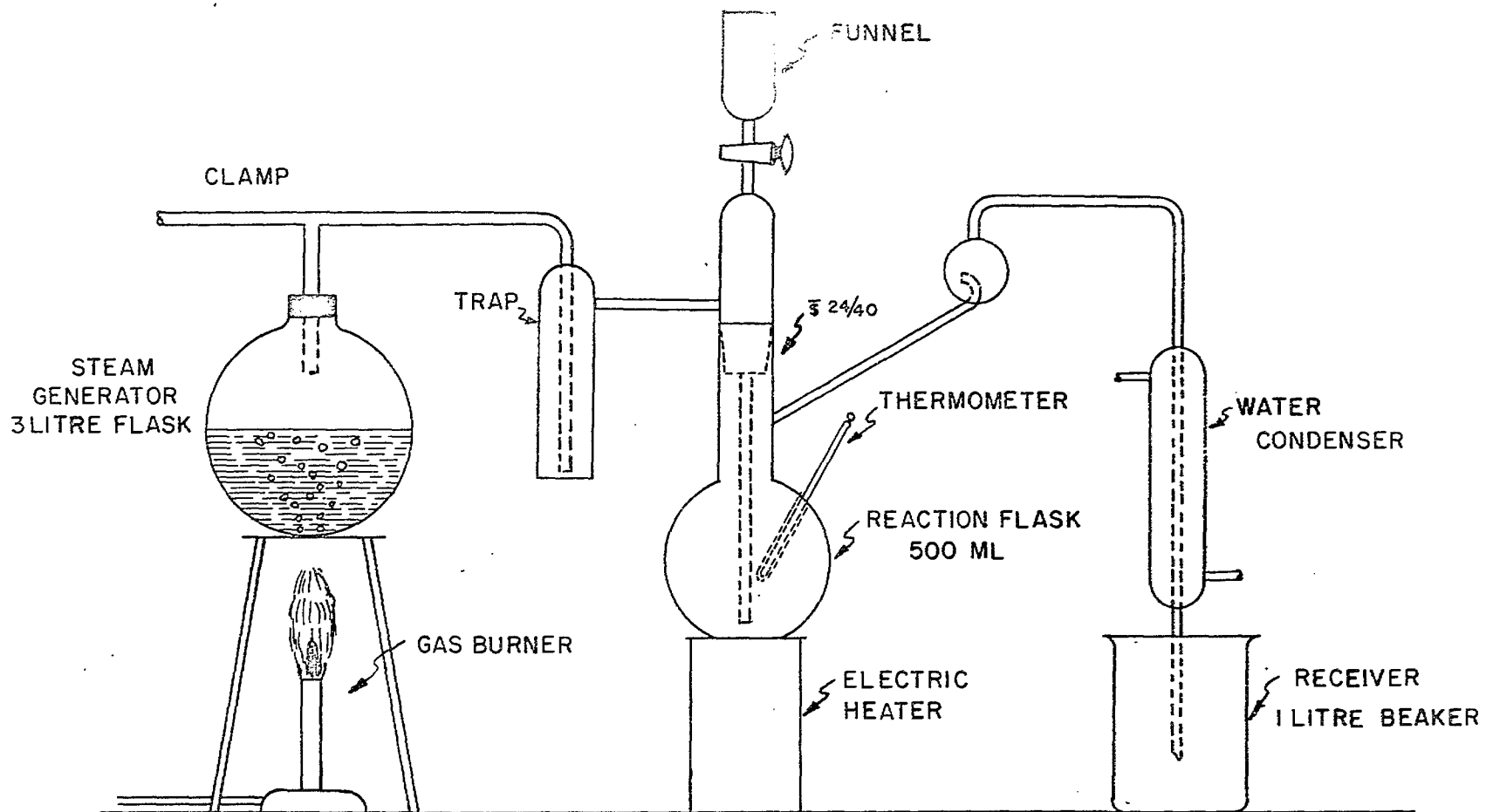


Figure 5 - Steam Distillation Apparatus

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

Sample weights of 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 water and 50 ml concentrated sulphuric acid are added through the funnel. The heater is turned on and when the temperature in the reaction flask reaches 135°C, steam is admitted to the reaction flask. 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 distillate, after removal from the system, is heated on a hot plate until the volume is less than 450 ml, cooled and then made up to 500 ml in a volumetric flask.

A reagent blank solution is prepared by the above procedure and is treated under the same conditions as the samples. Suitable aliquots can then be taken for a colorimetric determination. The standard curve is prepared by using similar aliquots of the blank solution and adding aliquots of potassium chloride stock solution.

The background effect was lower in the steam distillation method because larger sample weights were used. This means that the quantity of background

chloride present in the aliquot required for colorimetric development was less than it was in the aliquots required from the leaching or fusion decomposition procedures.

The distillation - colorimetric procedure has been applied to three zinc oxide samples.

Comparison of Results

The comparison of the distillation - colorimetric procedure with the distillation - titration procedure (6) and with those involving a leaching or fusion prior to the colorimetric determination is shown in Table 2, where chloride was determined in three samples of zinc smelter products, ie zinc oxide, smelter stock dust and Moore residue (Samples I, II and III respectively).

The results, as shown in Table 2, indicate that the best procedure to be followed for the colorimetric analysis is the isolation of the soluble chlorides by steam distillation prior to the colorimetric procedure.

Concordant results were obtained when the soluble chlorides were isolated by steam distillation followed by a potentiometric titration.

The leaching and fusion techniques, followed by a colorimetric determination of the chlorides, are not reliable, due to background effect caused by the chlorides present in the reagents, which results in lack of precision in the reference curves and in erratic chloride values for unknown samples.

TABLE 2

Comparison of Determinations Following Various
Decomposition Procedures

Method of Sample Preparation and Analysis	% Chlorine		
	Sample I	Sample II	Sample III
Distillation - Colorimetric	(3)** 0.024 ± .003	(3) 0.024 ± .001	(3) 0.001 ± .0009
Distillation - Titration	(3) 0.027 ± .001	(3) 0.026 ± .004	(3) 0.000 ± 0.000
Cold-water leaching* - Colorimetric	(1) 0.020	(1) 0.013	(1) 0.000
Na ₂ CO ₃ Fusion* - Colorimetric	(6) 0.052 ± .017	(6) 0.041 ± .012	(6) 0.021 ± .006
1% NaOH leaching* - Colorimetric	(2) 0.031 ± .001	(2) 0.033 ± .005	(2) 0.011 ± .002
KNO ₃ + Na ₂ CO ₃ fusion* - Colorimetric	(1) 0.045	(1) 0.033	(1) 0.042
NaNO ₃ + Na ₂ CO ₃ fusion* - Colorimetric	(1) 0.019	(1) 0.026	(1) 0.000

*Background effect possible.

**Bracketed figures indicate the number of determinations.

ACKNOWLEDGMENT

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