A New Spectrophotometric Method for the Determination of Small Amounts of Chloride Using the Mercuric Thiocyanate Method

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Introduction

A more rapid and accurate method for the determination of a very small amount of chloride ion in natural waters such as rain water, river waters, etc., has been desired.

An indirect colorimetric determination of chloride using solid silver chromate and diphenylcarbazide has been reported[1]. A small amount of chloride can also be estimated by the effect on suppression of reaction of mercuric ion with diphenylcarbazide or diphenylcarbazone[2]. K. Kuroda and E. B. Sandell[3] have studied a photometric method for the determination of chloride which is based on the formation of a colloidal suspension of silver sulfide by treatment of the ammoniacal solution of silver chloride with sulfide. Recently, chloride ion has been determined colorimetrically after exchanging for iodate ion with granular silver iodate in a column[4].

In the previous paper[5], the authors presented a new rapid colorimetric method for the determination of low concentrations of chloride using a very slightly ionizing mercuric thiocyanate solution and an iron alum solution. Chloride ion reacts with $Hg(SCN)_2$ to form $HgCl_2$, $HgCl_4^{2-}$, and SCN^-, which gives a reddish-orange color with ferric ion in nitric acid solution. The orange color of ferric thiocyanate ($FeSCN^{2+}$) formed in the solution is determined colorimetrically. The colored solution obtained has an absorption maximum at 460 mμ, and this colored substance is not extracted with ethyl ether[6]. The calibration curves (absorbance-concentration curves) do not show a linear relationship with the concentrations of chloride.

Lately we have found that the calibration curves of chloride conform to Beer's law at concentrations up to 50 p. p. m. when dioxane is used in the determination of chloride by the mercuric thiocyanate method. This improved spectrophotometric method for the determination of chloride, which is satisfactory for the range of 0.05–80 p. p. m. of chloride, is described in this report.

Experiments and Discussion

Reagents.—*Standard chloride solution* (1,000 p. p. m. Cl^-): 2.103 g. of potassium chloride (guaranteed reagent) was dissolved in 1 l. of distilled water. Solutions of suitable concentrations were prepared by diluting this stock solution.

Potassium Thiocyanate Solution.—About 10 g. of potassium thiocyanate (guaranteed reagent) was dissolved in 1 l. of water. This solution (about 0.1 M) was then standardized by the Volhard's method. Solutions of suitable concentrations were prepared by diluting this standard solution.

Solid Mercuric Thiocyanate.—When a potassium thiocyanate solution is added, drop by drop, to a mercuric nitrate solution containing nitric acid, using iron alum as an indicator, white crystalline $Hg(SCN)_2$ is precipitated. This precipitate is filtered off through a glass filter, and washed with cold water, and then dried in the air. Utilizing this procedure, solid mercuric thiocyanate was prepared. (This compound is stable for a long time.)

1,4-Dioxane (b.p. 102°C, m. p. 11.3°C, Dielectric const. 2.1).—Dioxane (guaranteed reagent) was used after being purified. Purification was accomplished by distilling with an adequate amount of metallic sodium, and collecting at 102°C.

Mercuric thiocyanate solution (*A*)* was prepared by dissolving 100 mg. of mercuric thiocyanate in 100 cc. of a mixed solvent consisting of 9 volumes of dioxane and 1 volume of absolute ethyl alcohol. The freezing point of this mixed solvent was about 4°C. Mercuric thiocyanate solution (B) was prepared by dissolving 100 mg. of mercuric thiocyanate in 100 cc. of a mixed solvent consisting of 2 volumes of dioxane and 1 volume of alcohol. Mercuric thiocyanate solution (C)[5] was prepared by dissolving 300 mg. of mercuric thiocyanate in 100 cc. of alcohol. All these mercuric thiocyanate solutions mentioned above were stable.

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1) F.D. and C.T. Snell, "Colorimetric Methods of Analysis", (1949) Vol. II, p. 715; K. Imai, *J. Japan Biochem. Soc.*, **20**, 147 (1948).

2) Yu. Yu. Luré and Z. V. Nikoraeva, *Zavodskaya Lab.*, **12**, 161 (1946); *C. A.*, **40**, 7070 (1946); S.M. Drachev and F.I. Ginzburg, *J. Applied Chem.* (*U.S.S.R.*), **11**, 879 (1938); F. E. Clark, *Anal. Chem.*, **22**, 553 (1950).

3) K, Kuroda and F.B. Sandell, *Anal. Chem.*, **22**, 1144 (1950).

4) J.L. Lambert, S.K. Yasuda, *Anal. Chem.*, **27**, 444 (1955).

5) I. Iwasaki, S. Utsumi and T. Ozawa, This Bulletin, **25**, 226 (1952). S. Utsumi, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **73**, 835, 838 (1952).

6) I. Iwasaki and H. Shimojima, ibid., **76**, 749 (1955). H.S. Frank and R.L. Oswalt, *J. Am. Chem. Soc.*, **69**, 1321 (1947).

* Mercuric thiocyanate is difficultly soluble in cold water and dioxane, but more soluble in ethyl alcohol.

Iron alum solution (A) was prepared by dissolving 8 g. of ferric ammonium sulfate (guaranteed reagent) in 100 cc. of 6 N nitric acid, free from chloride. Iron alum solution (B) was prepared by dissolving 6 g. of ferric ammonium sulfate in 100 cc. of 6 N nitric acid. Iron alum was used as a reagent of ferric ion, because it is easily obtained in the purely crystallized state, free from chloride, whereas ferric nitrate is hygroscopic and often contains chloride.

Apparatus.—Absorption measurements were carried out with a Beckman Model DU spectrophotometer using 10 mm. cells at 460 mμ.

Effect of Dioxane.—The influence of the addition of dioxane upon the colorimetric determination of chloride by the mercuric thiocyanate method was studied. Results obtained are shown in Fig. 1, in which line (I) corresponds to the calibration curve of chloride obtained by the former method5) reported previously. The experiments were carried out under the following conditions: 10 cc. of the sample solution were pipetted into a test tube equipped with a glass stopper. Then 2 cc. of iron alum solution (B) and 1 cc. of mercuric thiocyanate solution (C) were added. The absorbances were plotted against the concentrations of chloride at 20°C, ten minutes after mixing.

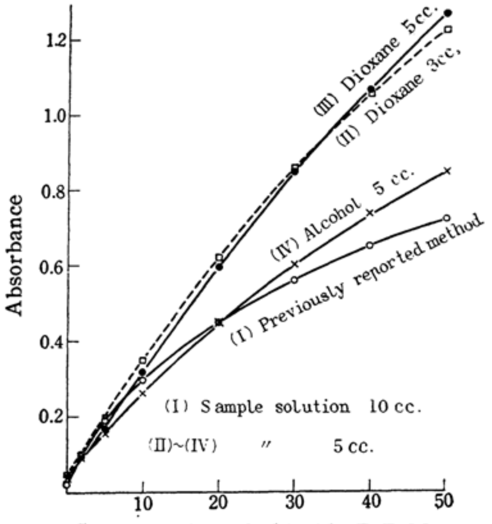

Fig. 1. Absorbance-concentration curves and effect of dioxane and alcohol at 460 mμ, 20°C.

As will be seen in Fig. 1, the calibration curve (I) was not linear with respect to the concentrations of chloride. When 2 cc. of iron alum solution (B), 1 cc. of mercuric thiocyanate solution (C) and then 3 cc. of dioxane were added to 5 cc. of the sample solution, the absorbance-concentration curve shown in the broken line (II) was obtained. When 5 cc. of dioxane, and ethyl alcohol were added respectively instead of 3 cc. of dioxane, the calibration curves corresponding to line (III) and (IV) respectively were obtained.

In this mercuric thiocyanate method, it is clear that the intensity of the color obtained is markedly affected by the addition of dioxane, but not of alcohol. The calibration curve of line (III) can be seen to conform nearly to Beer's law. After preliminary experiments the authors established a new spectrophotometric method available for the determination of chloride over the range of 0.05 to 80 p. p. m. of chloride.

Determination for a Range of 3 to 80 p.p.m. of Chloride.—Procedure (A).—To 2.5 cc. of the sample solution, 1 cc. of iron alum solution (A) and 3 cc. of mercuric thiocyanate solution (A) were added. The absorption measurements were carried out with a Beckman Model DU spectrophotometer using 10 mm. cells ten minutes after mixing.

Absorption Spectral Curves.—The absorption of the colored solutions (blank test, 10 and 30 p. p. m. Cl$^-$) was measured over the range of 390–600 mμ; absorbance was plotted against wave length in Fig. 2, in which there is one absorption maximum at 460 mμ. In addition, the solution has an absorption below 430 mμ, owing to the formation of a yellow ferric sulfate complex ion.

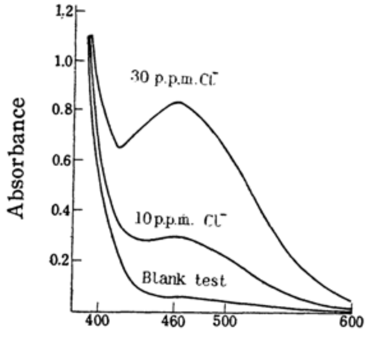

Fig. 2. Absorption Curves.

Time of Standing and Stability of Color.—Constant absorbance values of colored solutions (blank test, 10 and 30 p. p. m. Cl$^-$) were obtained after then minutes at room temperature (about 10°C). The color of the solution was stable. The results obtained are shown in Table I.

TABLE I

TIME OF STANDING AND STABILITY OF COLOR AT ABOUT 10°C

Time	Absorbance		
	Blank test	10 p. p. m. Cl$^-$	30 p. p. m. Cl$^-$
2 min.	0.065	0.285	0.824
3 〃	0.055	0.280	0.810
4 〃	0.051	0.275	0.801
5 〃	0.050	0.272	0.799
10 〃	0.050	0.272	0.791
15 〃	0.050	0.272	0.791
1 hr.	0.050	0.273	0.793
3 〃	0.050	0.272	0.793

Calibration Curves and Effect of Temperature.—The calibration curves shown in Fig. 3 were prepared by the Procedure (A) mentioned above using standard chloride solutions of known concentrations at 10°, 20° and 30°C. As will be seen in Fig. 3, the calibration curves show good agreement with Beer's law over the concentration range of 2–50 p. p. m. of chloride. But, for the concentrations higher than 50 p. p. m. of chloride, and lower than 2 p. p. m., the calibration curves do not show linear relation-ships, curving very slightly as shown in Fig. 3.

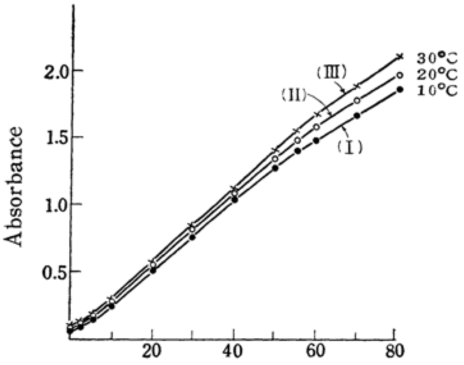

Fig. 3. Calibration curves and effect of temperature, at 460 mμ.

Since absorbance is considerably affected by temperature, as shown in Fig. 3, it is necessary to measure the absorbance under the same conditions of temperature in order to determine the concentration of chloride with good accuracy by this method. For the determination of concentrations lower than 3 p. p. m. Cl^-, the Procedure (B) described later in this report should be used.

A faintly colored blank solution was obtained when redistilled water was treated. The absorbance of the blank test was small, but constant, and was probably due to the dissociation of mercuric thiocyanate. The calibration curves shown in Fig. 3 were reproducible within ±1% for the range of 5–80 p. p. m. Cl^-.

Effect of the Reagent Concentrations.—The absorbance was affected by the amounts of mercuric thiocyanate solution and the concentrations of iron alum reagents. The experimental results obtained are shown in Fig. 4, in which line (I) corresponds to the calibration curve for line (II) in Fig. 3, and lines (II) and (III) show the experimental results obtained under the following conditions: for line (II), to 2.5 cc. of sample solution, 1 cc. of iron alum solution (B) and 3 cc. of mercuric thiocyanate solution (A) were added; for line (III), to 2.5 cc. of sample solution, 1 cc. of iron alum solution (A) and 2.5 cc. of mercuric thiocyanate solution (A) were added.

As will be seen in Fig. 4, it is necessary to use 3 cc. of mercuric thiocyanate solution (A) for 2.5 cc. of the sample solutions. On the other hand, when the amount of iron alum is increased, the color obtained is deeper, as in the case reported previously5).

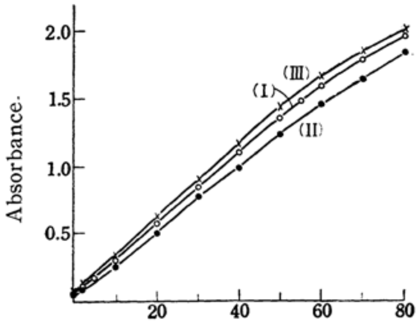

Fig. 4. Absorbance-concentration curves. Effect of the reagent concentration at 460 mμ. 20°C.

(I) $Hg(SCN)_2$ Soln. (A) 3 cc.
Fe-Alum Soln. (A) 1 cc.
(II) $Hg(SCN)_2$ Soln. (A) 3 cc.
Fe-Alum Soln. (B) 1 cc.
(III) $Hg(SCN)_2$ Soln. (A) 2.5 cc
Fe-Alum Soln. (A) 1 cc.

In this method the color intensity was slightly affected by the concentration of nitric acid. The effect of the concentration of nitric acid in iron alum reagent on this colorimetric method was observed in the presence of 30 p. p. m. of chloride at 15°C. The results obtained are shown in Table II.

TABLE II

EFFECT OF THE CONCENTRATION OF NITRIC ACID

Concns. of HNO_3 (N)	5	5.5	6	6.5	7
Absorbance	0.760	0.788	0.815	0.836	0.860

When the concentration of nitric acid was increased, the reddish-orange color became deeper.

Color Reaction.—In order to explain this color reaction some experiments were carried out. The results obtained are shown in Fig. 5, in which the line (I) corresponds to the calibration curve (II) in Fig. 3, and the other lines are obtained under the following conditions: for broken line (II), to 2.5 cc. of standard thiocyanate solutions of known concentrations, 1 cc. of iron alum solu-

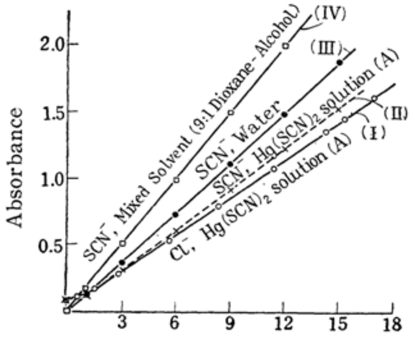

Fig. 5. Absorbance-concentration curves. Equilibrium of the color reaction.

tion (A) and 3 cc. of mercuric thiocyanate solution (A) were added; for line (III), to 2.5 cc. of the thiocyanate solution 3 cc. of distilled water and 1 cc. of iron alum solution (A) were added; and for line (IV), to 2.5 cc. of the thiocyanate solution, 1 cc. of iron alum solution (A) and 3 cc. of mixed solvents consisting of 9 volumes of dioxane and 1 volume of alcohol were added. The absorbances were plotted against the concentrations in 10^{-4} moles per liter at 20°C.

The calibration curve for chloride (line (I)) falls approximately along the calibration curve for thiocyanate (line (II)) containing the same amounts of mercuric thiocyanate solution. This fact indicates that the following reaction takes place from left to right almost completely.

$$2Cl^- + Hg(SCN)_2 \rightleftarrows HgCl_2 + 2SCN^-$$

The liberated SCN^- reacts with Fe^{3+} to give a reddish-orange color, as follows:

$$SCN^- + Fe^{3+} \rightleftarrows FeSCN^{2+}$$

The fact that the orange color of ferric thiocyanate formed in the solution becomes stronger in the presence of dioxane seems to indicate that the equilibrium of the above equation is largely shifted from left to right (lines (III) and (IV)). On the other hand, the difference between line (II) and (IV) seems to be due to the formation of mercuric thiocyanate complex ion[7] as follows:

$$n\,SCN^- + Hg(SCN)_2 \rightleftarrows [Hg(SCN)_{2+n}]^{n-}$$

Determination for a Range of 0.05 to 5 p.p.m. of Chloride.—The determination of lower concentrations of chloride was carried out by the following Procedure (B).

Procedure (B). Five cubic centimetres of the sample solution were pipetted into a test tube equipped with a glass stopper. Then 1 cc. of iron alum solution (A) and 1.5 cc. of mercuric thiocyanate solution (B) were added.

Calibration Curves and Effect of Temperature.—The calibration curves, (I) and (II) in Fig. 6, were prepared by Procedure (B) described above using standard chloride solutions of known concentrations at 15°C and 25°C respectively. Line (III) corresponds to the calibration curve obtained by the previously reported method[5] at 15°C (i.e., to 10 cc. of the sample solution, 2 cc. of iron alum solution (B) and 1 cc. of mercuric thiocyanate solution (C) were added). These calibration curves in Fig. 6 show good agreement with Beer's law over the range 0.05–3 p.p.m. of chloride.

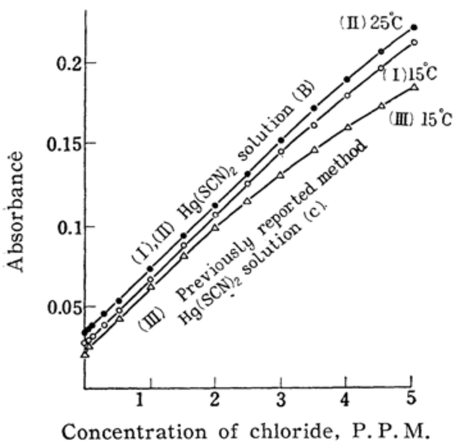

Fig. 6. Calibration curves for the lower range of chloride (I—II).

These curves were affected slightly by temperature as will be seen in Fig. 6. The absorbance of the blank test was very small, but constant. The lowest concentration of the standard solution whose color could be distinguished from that of the blank test was 0.05 p.p.m. Cl^- (1.4×10^{-6} M). The calibration curves shown in Fig. 6 were reproducible within ±0.05 p.p.m. Cl^-. In this method a better result will be obtained by the use of 100 mm. cells instead of 10 mm. cells. Especially in the determination of lower concentrations of chloride, the operator must be properly careful of contamination from outside.

Effect of Various Ions.—Bromide, iodide, cyanide, sulfide and thiosulfate react with $Hg(SCN)_2$ solution to liberate SCN^- ion, which gives a reddish-orange color with ferric ion in the same way as chloride[8], even in this improved method. Among the substances which interfere intrinsically with this method, sulfide, thiosulfate, cyanide, and thiocyanate are destroyed by heating with hydrogen peroxide in alkaline solution[9].

The effect of various ions except the interfering ions described above on this method (Procedure A) was examined in the presence of 30 p.p.m. Cl^- and blank test. Some of the results obtained are given in Table III.

TABLE III

EFFECT OF IONS ON PROCEDURE (A) AT 15°C

Substance	Concentration	Absorbance	
	p.p.m.	Blank test	30 p.p.m. Cl^-
None	0	0.053, 0.053	0.815, 0.813
$NaNO_3$	85,000 (1 M)	0.070	0.907
〃	8,500 (0.1 M)	0.053	0.818
SO_4^{2-}	5,000	0.052	0.738
〃	500	0.053	0.813
H_2O_2	1,000 (0.1%)	0.053	0.813
PO_4^{3-}	100	0.048	0.772
〃	10	0.053	0.815
F^-	100	0.052	0.793
〃	10	0.053	0.807
Ca^{2+}	1,000	0.053	0.818
Al^{3+}	1,000	0.053	0.815
Cu^{2+}	100	0.053	0.813
Ba^{2+}	100	0.053	0.818
Cr^{3+}	100	0.053	0.815
Fe^{3+}	100	0.054	0.821

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[7] F. Gallais and J. Mounier, *Compt. rend.*, **223**, 722, 790 (1946).

[8] S. Utsumi, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **73**, 889 (1952); ibid., **74**, 32, 301 (1953).

[9] S. Utsumi, ibid., **74**, 608 (1953); I. Iwasaki, S. Utsumi and T. Ozawa, This report was presented at a symposium of the Japan Soc. for Anal. Chem. May, 1953.

Substance	Concentration	Absorbance	
		Blank test	30 p. p. m. Cl^-
None	p. p. m. 0	0.053, 0.053	0.815, 0.813
Fe^{2+}	100	0.053	0.818
Ni^{2+}	100	0.052	0.813
Co^{2+}	100	0.053	0.815
SO_3^{2-}	100	0.053	0.813
NO_2^-	100	0.053	0.815
ClO_4^-	100	0.053	0.815
ClO_3^-	100	0.052	0.813
BrO_3^-	100	0.777	1.523
〃	10	0.103	0.903
IO_3^-	100	0.053	0.886
〃	10	0.053	0.815
$[Fe(CN)_6]^{4-}$	10	0.255	0.824
〃	1	0.063	0.815
$[Fe(CN)_6]^{3-}$	10	0.130	0.830
〃	1	0.060	0.815

The experimental results are summarized as follows:

(1) Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, acetate and silicate (calculated as SiO_2) ions have no effect even when found to be of the magnitude of 1,000 p. p. m.

(2) Cu^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Ti^{4+}, Ce^{3+}, Th^{4+}, Bi^{3+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, SO_3^{2-}, AsO_4^{3-}, BO_2^- and $C_2O_4^{2-}$ ions do not interfere when the concentration is as high as 100 p. p. m. Since a precipitate is formed in the case of barium, it should be centrifuged off in order to remove it. The color of Cu^{2+}, Cr^{3+}, Ni^{2+} and Co^{2+} ions is negligible up to 100 p. p. m. in this method.

(3) Sodium nitrate** does not interfere when present even in the amount of 0.1 M (8,500 p. p. m.); but at a very large concentration higher results are obtained.

(4) 500 p. p. m. of sulfate do not interfere; but 5,000 p. p. m. give lower results probably due to the reaction with ferric ion.

(5) 10 p. p. m. of fluoride and phosphate do not interfere; but 100 p. p. m. give lower results probably owing to the formation of complex ion with ferric ion.

(6) The presence of nitrite at the concentration of 100 p. p. m. does not interfere at 15°C, but at 30°C a slight interference is observed.

(7) Hydrogen peroxide does not interfere at 0.1% (1,000 p. p. m.).

(8) 100 p. p. m. of chlorate and perchlorate, and 10 p. p. m. of iodate do not interfere; but 10 p. p. m. of bromate and 100 p. p. m. of iodate give higher results.

(9) Ferrocyanide and ferricyanide interfere when present in small amounts.

As mentioned above, interfering substances are few. Bromide, iodide, cyanide, thiocyanate, sulfide, thiosulfate, bromate, ferrocyanide and ferricyanide interfere; but they are not usually present in natural waters in such concentrations as would give a serious error. This rapid and accurate spectrophotometric method for the determination of a small amount of chloride can possibly be applied widely to the determination of chloride in rocks[10], natural waters[11] and metals[12].

Summary

A new spectrophotometric method suitable for the determination of a small amount of chloride using iron alum solution in nitric acid solution, and mercuric thiocyanate solution in a mixture of dioxane and alcohol solution has been established.

The calibration curves conform to Beer's law at concentrations up to 50 p. p. m. of chloride. The calibration curves are reproducible within ±1% for the range of 5–80 p. p. m. Cl^- (Procedure A), and within ±0.05 p. p. m. for the range of 0.05–5 p. p. m. Cl^- (Procedure B). As the calibration curves are affected by temperature, it is necessary to measure the absorbance always under the same conditions of temperature in order to achieve good accuracy.

The colored solution is stable. A very small volume of the sample solution such as 5 cc. or 2.5 cc. is good enough for the determination. Interfering substances are few, because this method is carried out in acid medium. Br^-, I^-, CN^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, BrO_3^-, $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ interfere, but usually they are not present in natural waters in concentrations that would give a serious error.

This simple method is suitable for rapid determinations, because it is unnecessary to control pH or filter the precipitate. It is suggested that this method can be widely applied to the determination of chloride in waters, rocks, etc.

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** For the determination of chloride in silicate rocks, large amounts of sodium nitrate are formed[10].

[10] I. Iwasaki, T. Katsura and N. Sakato, *J. Chem. Soc. Japan* (*Pure Chem. Sect.*), **76**, 1116 (1955).

[11] I. Iwasaki, T. Nitta and T. Tarutani, ibid., **74**, 1003 (1953).

[12] I. Iwasaki, T. Tashiro and T. Ozawa, *Japan Analyst*, 5, 275 (1956).