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Spectrophotometric Determination of Chloride Ion.

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SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDE ION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
The Department of Chemistry

by
Hans Coll
M.S., Louisiana State University, 1955
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Methods for the quantitative determination of chloride ion have been reviewed. A direct spectrophotometric method with iron(III) perchlorate as the reagent has been developed. This method is based on the formation of the monochloro complex of iron(III) in solutions of appreciable perchloric acid concentration. Chloride ion may be determined in a concentration range of 4 to 50 p.p.m. by measuring the absorbancy of the complex around 350 mμ. Interferences from other ions are not significant, and the determination may be carried out in the presence of other halides. The usefulness of the spectrophotometric method in water analysis has been demonstrated in a comparative study with standard titrimetric procedures. The method has further been adapted for the determination of chloride in air.

The complex FeCl₃⁺ has been identified as the species responsible for the absorption band at 350 mμ. Apparent stability constants of this complex have been determined at various concentrations of perchloric acid. It was found that the stability constant (K) increased from 4.2 (in 2.5 M acid) to 6.1x10³ (in 9.0 M acid). Solutions which contained blends of perchloric acid with sodium and magnesium perchlorate, respectively, were in-
cluded in this study. A plot of log \( K \) vs. perchlorate ion concentration resulted in separate curves for the acid and the salt blends. From the change of \( K \) with temperature, standard enthalpy and entropy changes have been determined for solutions of 3.0 and 8.5 M perchloric acid. A partial explanation for the dependance of the stability of the chloro complex on the composition of the medium has been given in terms of the dehydrating action of perchlorates.

With regard to the findings of this investigation the existence of iron(III) perchlorato complexes appears to be questionable.

A brief discussion of the photosensitivity of iron(III) complexes has been given. Photoreduction of iron(III) and formation of Cl as a result of electron transfer from ligand to central atom explains the disappearance of the complex upon exposure to light, an effect, which was found to be more pronounced at higher acid concentrations.
CHAPTER ONE
THE QUANTITATIVE DETERMINATION OF CHLORIDE

Chloride ion, the most abundant of the halides, is a common constituent of the earth's crust. The solubility of chlorides—particularly the chlorides of the alkali metals and alkaline earth metals—accounts for its appreciable concentration in natural waters. The amount of chloride in the solid crust of the earth (lithosphere) has been estimated as 0.055%, while the value for the hydrosphere has been given as 20.7%. Free chlorine, except occasionally in volcanic exhalations, is rarely ever encountered in nature. Chlorine, predominantly in the form of chloride ion, exerts a variety of important biological functions and is found in all animals and almost in all plants. Free chlorine, and particularly organic and inorganic derivatives of the element, play an important role in a large number of technological processes.

From the standpoint of the analytical chemist, chloride ion occupies a central position among all species derived from chlorine, partly because it frequently occurs, but also because the ion represents the stable product obtained by reduction of chlorine gas and decomposition of organic chloro compounds.
Qualitative tests for chloride ion are primarily based upon the insolubility of silver chloride or mercury(I) chloride, or upon the oxidizing power of chlorine gas which is obtained by oxidation of chlorides. Solid samples may be analyzed for chloride by treatment with concentrated sulfuric acid and potassium dichromate; volatile chromyl chloride is distilled from the reaction vessel and the presence of chloride is established by a positive test for chromate in the receiver. None of these reactions is specific. Most of them suffer from interferences by bromide and iodide, although special techniques, such as successive elimination by selective oxidation and extraction, may permit the identification of these ions in the presence of each other.

The majority of the classical procedures for the quantitative determination of chloride ion likewise employ silver nitrate: The gravimetric method, which is the oldest one, and argentimetric titrations have found a wide application. According to Mohr\textsuperscript{35} the end-point of the titration may be indicated by the formation of reddish-brown silver chromate in neutral solution. Fajans and Wolff\textsuperscript{17} proposed the application of adsorption indicators of the fluorescein series. In the method of Volhard\textsuperscript{57} an excess of standard silver nitrate solution is added to the unknown and back-titrated with standard thiocyanate solution; iron(III) ammonium sulfate, which forms the red thiocyanato complex with the first drop of excess thio-
cyanate, is used as the indicator. The end-point is sharper than in the Mohr method, but an error may be introduced by the adsorption of silver ion on freshly precipitated silver thiocyanate.\(^\text{25}\)

For more than a century the mercurimetric titration, illustrated by the equation

\[ \text{Hg}^{2+} + 2 \text{Cl}^{-} \rightarrow \text{HgCl}_2, \]

has been applied for the quantitative determination of chloride ion. Early investigators used turbidimetric indicators. A more satisfactory indicator was introduced by Dubsky and Trtilek\(^\text{13}\) who reported the successful application of diphenylcarbazide and diphenylcarbazone for the detection of the end-point. Further modifications and improvements have been elaborated by Clarke\(^\text{14}\), Parsons and Yoe,\(^\text{38}\) and by Smit.\(^\text{47}\)

Lur'e and Nikolaeva\(^\text{34}\) developed a sensitive colorimetric procedure by measuring the color-suppressing effect of chloride ion upon mercury(II) diphenylcarbazide.

Several other indirect procedures employ silver thiocyanate as the reagent. Iodate ion is liberated according to

\[ \text{AgIO}_3 + \text{Cl}^{-} \rightarrow \text{AgCl} + \text{IO}_3^-. \]

The precipitate is removed by filtration and iodate ion is subsequently determined manometrically,\(^\text{43}\)

\[ 2 \text{IO}_3^- + 3 \text{N}_2\text{H}_4 \rightarrow 2 \text{I}^- + 6 \text{H}_2\text{O} + 3 \text{N}_2, \]

titrimetrically with thiosulfate after addition of iodide,\(^\text{45}\) or colorimetrically,\(^\text{46}\) iodate is reacted with iodide and the yellow color of \(\text{I}_3^-\) is measured directly.
wise, the blue color produced upon addition of starch can be used for colorimetric estimation. These methods have attracted special attention in biological work.\textsuperscript{50, 56}

Avalani\textsuperscript{2} has described a microdetermination based upon the analogous reaction between chloride ion and mercury(I) iodate. A modification of the silver iodate method is given by the work of Lambert and Yasuda\textsuperscript{32} who passed the chloride solution through a column packed with silver iodate followed by colorimetric measurement of the blue complex formed in the reaction between iodate ion, cadmium iodide, and linear starch.

Other indirect methods have been published by Duval and Mazars\textsuperscript{14} -- an exchange reaction between chloride and silver ferrocyanide and subsequent colorimetric estimation of ferrocyanide --, and by Zall, \textit{et al.}\textsuperscript{63} The work of the latter represents an improvement of a procedure earlier developed by Utsumi,\textsuperscript{55} who colorimetrically measured the amount of iron(III) thiocyanate formed in the reaction

\[
\text{Hg(CNS)}_2 + 2 \text{Cl}^- \rightarrow \text{HgCl}_2 + 2 \text{CNS}^{-} \\
\text{CNS}^- + \text{Fe}^{+++} \rightarrow \text{Fe(CNS)}^{++}.
\]

Snell\textsuperscript{49} mentions a similar exchange reaction between chloride ion and silver chromate, in which chloride is estimated from the amount of chromate released; the latter may be determined by any of the conventional methods. An interesting variation of this method, adapted for microanalysis, consists of measuring the time required for the transformation of silver chromate to silver chloride.\textsuperscript{36} An indirect
A colorimetric method which employs silver nitrate, thiocyanate, and ferric ion as the reagents has been proposed by Hettche.\textsuperscript{24}

Several procedures which involve oxidation to chlorine have been developed. Brinkley\textsuperscript{7} oxidized with potassium persulfate in dilute phosphoric acid and colorimetrically measured the quantity of the red oxidation product which chlorine forms with brucine. Modifications of this reaction permit the differentiation between chloride, bromide, and iodide.

Potentiometric titrations of chloride may be performed with a silver-silver chloride electrode employed for indication.\textsuperscript{61} A rotating micro electrode for this purpose has been described by Brueggemann.\textsuperscript{9}

The nephelometric determination of chloride as silver chloride was originated by Richards and Wells.\textsuperscript{43} Improvements of this method are due to the work by Lamb, \textit{et al.},\textsuperscript{31} and more recently by Luce, \textit{et al.}\textsuperscript{33} The sensitivity achieved is considerable; Yoe\textsuperscript{62} mentions the development of a "weak turbidity" with solutions containing $5 \times 10^{-6}$ equivalents of chloride ion per liter. Kolthoff and Yutzy\textsuperscript{30} have published a critical study on the nephelometric procedure.

A very recent publication deals with the direct spectrophotometric determination of halide ions with palladium(II) sulfate as the reagent.\textsuperscript{10} The authors measured the absorbancy due to the bromo and chloro complexes of palladium(II) at 230 mp, and the iodo complex at 390 mp.
Of all the methods listed the titrimetric procedures with silver nitrate and mercury(II) nitrate still find by far the widest application, although the modern trend in general favors optical methods. The limited acceptance of photometric chloride procedures may be explained by the fact that most of the optical methods enumerated are indirect, and therefore usually neither simple nor reliable. The same holds true for the nephelometric determination; although here the procedure may appear simple, difficulties arise in the development of precipitates with comparable light-scattering properties (particle size). The direct spectrophotometric method with palladium(II) sulfate as the reagent is too new to be commented on, but its general applicability does not seem to be likely because of the unfavorable wave length of 230 μm at which the absorption peak of the complex occurs.
CHAPTER TWO
DIRECT SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDE
WITH IRON(III) PERCHLORATE

In view of the shortcomings of conventional procedures a method is proposed which in several respects appears to be superior to the procedures applied in the past for the quantitative determination of chloride ion.

For some time it has been known that iron(III) is not yellow, as popularly believed, but instead is essentially colorless. The yellow color attributed to iron(III) is actually due to chloro or hydroxo complexes of iron. The light-absorption properties of the chloro complexes suggested the possibility of using chloride-free iron as the reagent for the colorimetric estimation of chloride and an investigation was undertaken to ascertain the validity of a direct spectrophotometric procedure based on such an approach.

Although iron(III) chloro complexes do absorb radiant energy in the visible portion of the spectrum, the greatest absorption is in the ultraviolet. It was found that the intensity of the absorption band exhibited by the complex at 350 μ greatly depends on the amount of acid present. For reasons of sensitivity it was, therefore, desirable to maintain an acid concentration as high as possible and work in
the ultraviolet rather than in the visible portion of the spectrum.

Addition of a moderate amount of strong acid was also found necessary for preventing the formation of hydroxo complexes of iron(III) which heavily absorb light in the near ultraviolet. Among the strong acids available, sulfuric acid could not be used for acidification because of the formation of iron(III) complexes with interfering spectral characteristics. Likewise, nitric acid at higher concentrations caused interferences. Perchloric acid appeared to be most suitable. In the presence of this acid, iron(III) exhibits only a very low absorbancy in the spectral range appropriate for the determination of chloride.

Under the conditions employed in these studies, no decomposition of perchloric acid was evidenced at any time. No reduction to chloride was ever observed nor were there any indications of other interfering or hazardous reactions. The procedures involved must be considered as perfectly safe.

APPARATUS AND REAGENTS

A Beckman Model DU spectrophotometer with matched 1 cm. silica cells was used for most of the studies; a tungsten lamp served as the light source. It was established that a Model B spectrophotometer and Corex cells are likewise suitable for this work. Absorption spectra were recorded by means of a Beckman Model DK-1 recording spectrophotometer.
A Machlett closed-system buret (10 ml), connected with a large stock bottle by an all-glass conduit, was used for delivering exact volumes of perchloric acid. Drying tubes filled with anhydrous magnesium perchlorate protected the acid from moisture. The buret should have a close fitting glass stopcock to minimize leakage of perchloric acid. All stopcock lubricants studied were found to be attacked by the acid upon prolonged contact and therefore the fit of the plug is of considerable importance.

It was observed that the absorbancies of the iron chloro complex in perchloric acid stronger than 5 M, decreased when exposed to bright light. The solutions were, therefore, protected from light by coating the volumetric flasks with black paint almost up to the mark, and by covering the necks of the flasks with small bags of opaque paper. Low actinic glassware gave incomplete protection against bright light.

Iron(III) perchlorate solutions were prepared from reagent grade ferric perchlorate (non-yellow) as supplied by G. F. Smith Chemical Company. Trace impurities of chloride present in the iron perchlorate were removed by treatment of the salt with small portions of 70% perchloric acid. The salt is only sparingly soluble in the acid, but the chlorides are readily dissolved and removed. In preparing iron perchlorate solutions, an approximate amount of the purified salt was dissolved in water or in perchloric acid, and the solution titrimetrically standardized by the potassium dichromate pro-
The solutions were then diluted to bring them to the desired strengths. Reagent grade perchloric acid (70-72% or 60% supplied by Baker and Adamson and by Mallincrodt, respectively) was found to be of satisfactory purity. The perchloric acid always seemed to be of a higher degree of purity than indicated by the manufacturer's assay.

A standard chloride solution was prepared by dissolving 1.314 g. of dried sodium chloride in one liter of distilled water. This solution had a Cl-titer of 0.800 mg. and was further diluted to yield solutions of appropriate chloride concentrations.

For evaluating the extent of interferences, solutions were prepared from reagent grade chemicals to contain known amounts of the ions listed in Table I. Solutions for anion interferences were prepared from sodium salts, those for cation interferences contained nitrate or perchlorate.

EXPERIMENTAL AND RESULTS

The effect of acid concentration on the absorbancy of solutions at a given concentration of chloride and ferric ion was studied. Small volumes of iron and chloride solutions were transferred to 10 ml. flasks, and varying amounts of 70% perchloric acid were added. The flasks were filled to the mark, shaken, and allowed to cool. At higher concentrations of acid the solutions were protected from light as described above. A study of absorption spectra of
various solutions differing in acid concentration disclosed a pronounced increase of absorbancy with acidity, accompanied by a shift of the absorption bands towards longer waves. The absorption peaks shifted by almost 15 μm when the perchloric acid concentration was increased from 2.5 to 8.5 M. A series of measurements were then carried out at 350 μm with solutions which contained 8 mg. per liter of chloride ion, 0.02 mole per liter of iron perchlorate, and perchloric acid concentrations varying from 2 to 10 M. Blanks of appropriate iron and acid concentrations were prepared, and the absorbancies of all solutions were measured with respect to water. The absorbancies due to the presence of chloride ion were calculated by subtraction of the corresponding blank values (Fig. 1, plot IIA).

The influence of iron concentration on the intensity of the absorption band was next studied. Two sets of measurements were carried out, one at 342 μm, the other at 350 μm (Fig. 2). The first set contained 17.5 mg. of chloride per liter in 6 M perchloric acid, the second one contained 8.00 mg. of chloride per liter in 8 M perchloric acid. The iron concentrations were varied from 0.001 to 0.1 M. Curves indicating the increase of background absorption with increasing concentration of iron are included in Figure 2.

It is evident from Figure 1 that increasing the concentration of perchloric acid beyond 8.5 M reduces the precision of the measurements because of the rise in background absorption without a corresponding increase in net
sensitivity. A practical limit is further set by the concentration of the commercially available perchloric acid. As indicated by Figure 2, a high concentration of iron(III) seems to be desirable if the simultaneous increase of blank absorption with iron concentration is disregarded. If 70% perchloric acid is used, a limitation of iron(III) concentration is set by the decreased solubility of iron perchlorate in the more concentrated acid.

A study of stability, temperature dependency, and adherence to the Beer-Lambert Law of the system was made by preparing a reagent which contained 0.139 mole of ferric perchlorate in one liter of 11.8 M perchloric acid. Transfer of 7.2 ml. of this reagent to a 10 ml. flask and dilution to the mark resulted in a solution 8.5 M with respect to perchloric acid and 0.01 M with respect to iron. Because of the hygroscopic properties of the perchloric acid this reagent had to be kept under anhydrous conditions. The specified volume of the reagent was delivered from the Machlett buret into flasks protected from light, and aliquots of standard sodium chloride solution were added. After dilution to the mark with distilled water the flasks were shaken and allowed to cool. The absorbancies of the solutions were measured at 353 mp with respect to a blank which contained corresponding amounts of acid and iron. A linear relationship between absorbancy and chloride concentration was established. The useful concentration range was found to be 1 to 12 mg. of chloride per liter (corresponding to absorban-
cies of 0.08 and 1.0 units). Because only one fourth of the total volume is available for the chloride solution, these figures have to be quadrupled to represent the useful concentration range for the unknown solution. The blank exhibited an absorbancy of approximately 0.06 unit with respect to distilled water. The influence of temperature was determined to be 1.4% per °C for the blank with respect to water, and -0.02% per °C for the sample with respect to the blank.

It was found that the absorbancies of solutions protected from light were constant for 100 hours. Exposure to bright light in uncoated flasks after addition of chloride caused a rapid decrease of absorbancies. During subsequent storing in the dark the absorbancies slowly increased although the original values were not again reached.

In order to test the reliability of the procedure, 21 solutions, each containing 5 mg. of chloride per liter, were measured with respect to blanks over a period of one week. The reagent as well as the volumetric equipment was the same in all experiments; corrections for changes in temperature were not applied. The values ranged from 0.428 to 0.449 absorbancy unit, the average being 0.440; the mean deviation was ±0.86%.

Interferences from a number of cations and anions were studied. Known amounts of potentially interfering ions were added to solutions containing 5 mg. of chloride per liter, and the difference from the theoretical value of
absorbancy was calculated. In studies on certain cation interferences where a substantial amount of nitrate ion was added, corrections were applied for the presence of this anion. The results are summarized in Table I, part 1. Where positive deviations due to interaction of iron(III) and interfering ions, independent from chloride concentration, could be assumed, the extent of interference is expressed as p.p.m. of interfering ions giving the same absorbancy as 1 p.p.m. of chloride. In other cases the extent of interferences is expressed as mg. per liter of interfering ion causing an error of 3% at a given concentration of chloride ion. Consideration was also given to the presence of potassium ion, iron(III) and perchloric acid. Interferences arising from bromides and iodides were studied in special detail. The presence of bromide ion caused the appearance of an absorption band at 420 mµ, probably due to the formation of a bromo complex with iron (Fig. 3). The ratio of absorbancies at 420 mµ and 353 mµ, $A_{420}: A_{353}$, was found to be 3.6 and was quite reproducible. The same ratio for chloride absorption was calculated to be 0.082. Thus it is possible to correct for bromides present in solution, provided no interaction with the chloro complex takes place. Results are presented in Table II.

By an analogous procedure the effect of iodides was studied. Iodide ion when added to the perchlorate reagent is oxidized to iodine. The resulting absorption spectrum is shown in curve 1 of Figure 3. When the iodide concen-
tration exceeded 200 mg. per liter, crystals of iodine were precipitated. These were removed by extraction into carbon tetrachloride. The spectrum of the iodine remaining in the aqueous phase appears to be essentially unaltered. It can be seen from Figure 3 that the absorbancy due to the presence of iodine drops to a low value around 353 m\(\mu\). Thus no extensive interference from iodides in a determination of chloride should be expected. A correction for iodides similar to the one applied for bromides is possible but is not considered necessary. Corrections for the presence of iodides and bromides simultaneously may be made by measuring the absorbancies of the solutions at 353, 420, and 470 m\(\mu\). Constants expressing ratios of absorbancies at different wave lengths are included in Table II. The constants for iodide appeared to be less reproducible than those for bromide. The constants listed in Table II will depend to a certain extent on the concentration of iron(III) and perchloric acid.

In order to dispense with the necessity of storing the reagent under anhydrous conditions, an alternative procedure was investigated. A reagent was prepared which contained 0.2 mole of iron(III) perchlorate in one liter of 5 M perchloric acid. Acid of this or lower concentration does not exhibit hygroscopic properties. The large amount of iron was chosen to compensate for the decrease in sensitivity resulting from the use of lower acid concentrations. Five ml. of this reagent--standardized with respect to acidity and iron concentration--were measured into 10 ml.
flasks and the features of this procedure were studied by experiments analogous to the ones described for the first procedure. The results may be summarized as follows. The plot of absorbancy against chloride concentration, measured at 348 mp, is linear; the workable range for 1 cm. cells corresponds to a concentration of 8 to 80 p.p.m. in the unknown. The absorbancy of the blank amounted to approximately 0.21 absorbancy unit. The temperature dependence was determined to be 3% per °C for the blank with respect to water, and as 1.3% per °C for the sample with respect to the blank. A statistical study on 20 solutions of constant composition gave a spread from 0.387 to 0.424, averaging 0.401 with a mean deviation of ±1.9%. If the absorbancy values were corrected for temperature (30°C), the spread was 0.404 to 0.416, averaging 0.408 with a mean deviation of ±0.6%. The absorbancy readings for the blank as well as for the sample were practically constant with time. After 50 hours a decrease of approximately 3% was observed. No effect due to exposure to light could be detected.

The results of interference studies are listed in Table I. The absorption bands arising from the presence of bromide and iodide (Fig. 3) appeared to be shifted towards the ultraviolet compared with the ones obtained by the first procedure; the iodine spectrum exhibits a second band around 340 mp. Extraction of precipitated iodine into carbon tetrachloride seems to have an effect on the spectrum of the aqueous phase (Fig. 3, plots 3 and 4). No attempt was
made to determine chloride in the presence of the other two halides, but it should be possible to apply corrections, as in the first procedure.

The preparation of the reagents, involving standardization of iron perchlorate solution and of perchloric acid can be simplified for practical work by preparing reagents of approximate strength, for which an individual chloride calibration curve can be established. Perchloric acid can be assumed to be of the concentration stated by the manufacturer, and the appropriate amount of iron(III) perchlorate can be weighed on a triple-beam balance. After treating this salt in the manner outlined below, almost twice the amount corresponding to the formula weight of iron perchlorate has to be taken to give solutions of desired concentrations, because of the large quantities of water and perchloric acid adsorbed on the crystals. Occasional checks by titration to establish the concentration of the ferric perchlorate solutions are recommended.

**Recommended Procedures**

Procedure 1. Shake 20 to 30 g. of reagent grade iron(III) perchlorate with small portions of 70% perchloric acid in a glass-stoppered flask. Decant the acid and repeat this operation until the acid layer no longer appears yellow. A coarse fritted-glass crucible of known weight is mounted on a suction flask, and the purified iron perchlorate is transferred to the crucible. The crystals are
pressed down with a glass rod flattened on one end, and the acid removed by suction. The crucible filled with iron perchlorate is then reweighed on a triple-beam balance; iron perchlorate is removed from the crucible until approximately 8 g. are left. This quantity is then dissolved in a few ml. of distilled water, and one liter of 70% perchloric acid is added. Perchloric acid, like iron perchlorate, is extremely hygroscopic and should be exposed to air as little as possible. The reagent is then transferred to a closed system buret which is protected from moisture by means of magnesium perchlorate drying tubes. Seven and four-tenths ml. of the reagent are accurately delivered to 10 ml. volumetric flasks which have been protected from light by a black coating. Two and one-half ml. of the unknown solution, to contain not more than 50 p.p.m. of chloride, are transferred to the flasks, and the solutions brought to volume with distilled water. The flasks are then shaken to mix the solutions, and after covering the necks of the flasks with a small bag of opaque paper, the solutions are allowed to cool. The absorbancies are measured at 353 μν with respect to a blank containing only reagent and distilled water. The concentration of chloride is determined by means of a calibration curve. A new calibration curve should be established every time a fresh reagent is prepared. If the reagent is to be kept over an extended period of time, occasional checks on the calibration curve are recommended.

Procedure 2. Approximately 120 g. of purified iron
perchlorate are dissolved in a mixture of 540 ml. of 60% perchloric acid and 460 ml. of distilled water. The reagent may be stored in a glass container without protection from moist air. Four and nine-tenths of this reagent are transferred to 10 ml. volumetric flasks. Five ml. of the unknown solution, to contain not more than 100 p.p.m. of chloride, are added and the flasks filled to the mark. The absorbancies of the solutions are measured at 348 mp with respect to a blank. The temperature of the solutions should be recorded, but it can be assumed that the temperature difference between sample and blank is insignificant. After correcting the absorbancy readings to the temperature at which the calibration curve had been established, the concentration of chloride is obtained from the curve. The correction for temperature is applied by adding to the absorbancy reading at temperature T the term 

\[(T_0 - T) \times A_T \times 0.013,\]

where \(T_0\) stands for the temperature at which the calibration curve was set up; \(A_T\) designates the absorbancy measured at temperature T.

**DISCUSSION AND CONCLUSION**

Procedures 1 and 2 present conditions for maximum sensitivity in a spectrophotometric determination of chloride with iron(III). Other procedures which employ a different concentration of perchloric acid and of iron(III) are quite conceivable. From the experimental results it is evident that differences exist between the systems in procedure 1.
Figure 4 shows the spectral bands of sample and blank in the two procedures. In determinations of chloride it was found more suitable to measure absorbancies at slightly higher wave lengths than correspond to the peaks of the respective absorption bands, because of the increase in background and extent of interference from certain substances with decrease in wave length.

Because of higher background, appreciable temperature dependence, and more extensive interference from certain common ions, such as sulfate, procedure 2 must be considered as inferior to procedure 1. Yet the advantages of procedure 2, the fact that no protection from humidity is required, and the insensitivity of the solutions towards light, should not be overlooked in practical work.

With the exception of mercury(II), a rather uncommon constituent, other ions do not seriously impair the applicability of procedure 1. Bromides and iodides, which account for heaviest interferences in most methods for the determination of chloride, may be tolerated in this procedure. Corrections for bromides are required if present in quantities above 30% of the chloride content. Iodides may be tolerated up to a twentyfold excess with respect to chloride, provided no precipitate of iodine is formed. Sulfate ion, up to a sixfold excess does not interfere (corresponding to a positive error of 3%). In procedure 2, on the other hand, interference from sulfate ion must be considered as more serious. Larger quantities of sulfate must be removed by
precipitation with barium perchlorate and subsequent centrifugation. Removal of sulfate ion by precipitation after iron-perchlorate reagent has been added, was found to be incomplete. Likewise, an error will be introduced if the unknown solution contains appreciable amounts of acid and iron(III). For a chloride concentration of 5 mg. per liter in procedure 1 the error will amount to 3% if the iron(III) concentration is increased from 0.010 to 0.014 M; the same effect is caused by an increase of perchloric acid concentration from 8.5 to 8.8 M. In procedure 2, at a chloride concentration of 8 mg. per liter, a 3% error is introduced by an increase of iron concentration from 0.100 to 0.102 M, or by an increase of perchloric acid from 2.50 to 2.55 M. These values represent a measure for the amounts of perchloric acid and iron(III) which may be tolerated in an unknown to be analyzed for chloride.

The main advantages of the method described in this paper over other methods presently in use for the determination of chloride lie in the simplicity and reliability of the procedures. Generally speaking, only nephelometric methods can be considered as more sensitive. An increase in sensitivity can be achieved by using longer cells. Yet, in view of the blank value it is advisable to limit the light-path to a maximum of 5 cm. Direct turbidimetric measurements (measurements of light transmitted by turbid samples) of silver chloride precipitates lead to a sensitivity only about 50% higher than is observed in Procedure 1.
Approximately the same relation of sensitivities is given for the direct spectrophotometric method with palladium(II) sulfate and the method described in this paper; but it can be asserted that in the case of the former, direct applicability is greatly impaired because at a wave length of 230 μ, where the absorption peak occurs, a large variety of interferences is to be expected. The indirect photometric determination of chloride with mercury(II) thiocyanate is approximately twice as sensitive as the iron perchlorate method. Dilution of the unknown (1:4) as necessitated by procedure 1, has been considered in this comparison of sensitivities. Therefore, the situation is even more favorable if the sensitivity is expressed in absolute quantities of chloride. Likewise, with respect to interferences, a comparison discloses several advantages of our method, particularly in the presence of other halogen ions.
CHAPTER THREE
DETERMINATION OF CHLORIDE ION IN WATER
A COMPARATIVE STUDY

Up to the present time three titrimetric procedures for the determination of chloride in water have been recommended as standard methods, namely the Mohr and Volhard titrations with silver nitrate and a mercurimetric determination. The purpose of this study is to illustrate some of the possible advantages of the spectrophotometric procedure over the existing standard methods, and to compare their performances in water analysis. Only the Mohr and the mercurimetric procedures were included in these comparative studies, because the Volhard method is more complicated, less accurate and less applicable for low concentration ranges of chloride ion.

PROCEDURES AND SOLUTIONS

Mohr Method

Reagents: As specified in "Standard Methods". ¹

Procedure: The titration was performed according to the standard procedure. ¹ In order to facilitate the observation of the end-points a yellow light source was used for illuminating the titration vessel.
Mercuric Nitrate Method

Reagents: As specified in "Standard Methods".

Procedure: The titrations were performed essentially according to the procedure outlined by "Standard Methods". It was found, however, that the end-point of the titration could be established more accurately through use of four blanks which contained the indicator and 0.05, 0.10, 0.15, 0.25 ml. respectively of mercuric nitrate standard solution. These blank values served as color standards for establishing end-points after difficulty was encountered when attempts were made to titrate to one specific color, because of the slow rate with which the reaction proceeded towards the end-point. It was found that 5 to 10 minutes may be required before the color intensity of the indicator reaches a maximum. The titration was performed at a moderate rate until the first tinge of purple appeared. The sample was set aside and after 15 minutes compared with the set of color standards. The excess volume of titrant was subtracted from the buret readings. The color standards were stabilized by the addition of gum arabic.

Spectrophotometric Method

Apparatus and reagents were the same as in the previous chapter, the procedure was the same as the one described as "Procedure 1".

A suspension of aluminum hydroxide can be used for clarification of turbid water samples. Potassium alum (125 g.) is dissolved in distilled water and precipitated
by addition of excess ammonium hydroxide. The precipitate should be made free of sulfate by repeated washing with distilled water and the final volume made up to 500 ml.

EXPERIMENTAL

A solution which contained 12.5 mg. of chloride in one liter of distilled water was analyzed in 25 runs under identical conditions by each of the three methods in accordance with the procedures given above. The purpose was to obtain information as to accuracy and precision of the methods at low concentrations of chloride under conditions favorable for the reproducibility of the results. Silver nitrate as well as mercuric nitrate titrants were standardized in 10 runs against a solution containing 2.00 mg. of chloride in 100 ml. Because of the small volumes of titrant consumed at these chloride levels a buret with 50 scale divisions per ml. was used. The runs were extended over several days. A calibration curve for the spectrophotometric method was established from 10 points covering a concentration range from 0.0075 mg. to 0.100 mg. of chloride per 10 ml. The absorbancies were measured by means of a Beckman Model B spectrophotometer (slit setting 0.55 mm.). The test runs were performed in groups of five. Distilled water was taken as the reference for the readings, and an average of 5 readings on blanks with respect to distilled water were subtracted. This somewhat unconventional procedure was justifiable from a statistical standpoint, because
a variation in one blank value would accordingly influence a whole set of measurements. A summary of results is presented in Table III.

Natural waters of various chloride concentrations were then used for comparative quantitative studies. Suspended material, if present, was first removed by filtration through coarse filter paper. In some cases the filtrate was still turbid and slightly colored and further clarification by means of aluminum hydroxide was employed prior to the spectrophotometric determinations. Exactly 7 ml. of water sample was transferred to a dry test tube and 0.5 ml. of aluminum hydroxide suspension added. The solution was stirred and centrifuged until all aluminum hydroxide had settled. An aliquot not to exceed 2.5 ml. was then taken for the determination of chloride and the final result was multiplied by a factor 7.5/7.0, the volume occupied by solid aluminum hydroxide being neglected. Table IV shows some typical results obtained by this treatment. The lowering of the absorbancies in those cases listed in Table IV must be considered as sufficient, because the spectrophotometric procedure involved further dilution, at least by a factor of 4. By tests of solutions of known chloride content it was ascertained that the treatment with aluminum hydroxide in the manner described did not cause any noticeable changes in the chloride concentration. Eight samples of natural waters were subjected to analysis by the three methods. Table V presents the results as obtained.
Finally, known amounts of chloride were added to two samples of natural waters whose chloride content had been determined previously (No. 1 and 5 in Table V). The chloride concentrations of the resulting solutions were calculated on the basis of the value determined by the spectrophotometric method. In the case of the solutions derived from No. 5, clarification with aluminum hydroxide was necessary. Accuracy and precision of the results in Table VI are only meaningful in the case of the spectrophotometric procedure (C); the titrimetric procedures (A and B) were only included as a check, and the results cannot be attributed the same weight as in case C because of the small number of runs or sample sizes which lead to a more extensive error.

DISCUSSION AND CONCLUSION

Several factors have to be considered in an attempt to interpret the results of this work with respect to precision and accuracy of the methods applied. The precision achieved in titrimetric analysis will to a certain extent depend on the skill of the experimenter, while in spectrophotometric work the results can be assumed as essentially unaffected by human factors; here the quality of the instrument is decisive for the precision of the measurements. With reference to the foregoing experiments it appears that the precision expressed as per cent deviation from the average is of comparable magnitude for all three methods. As to the titrations, it can be expected that the detection
of the end-points in a series of runs under identical conditions will give rise to small deviations only. The results derived from the spectrophotometric measurements may be considered as typical with respect to precision. The percentage error due to volumetric measurements (transfer of sample) will be higher in the spectrophotometric procedure, but even in this case should not be appreciable.

For low concentrations of chloride the precision of the Mohr titration has been estimated to be 0.1 mg. of chloride ion (corresponding to 0.2 ml. of titrant), and the precision of the mercuric nitrate method is given as \( \pm 0.05 \) mg. (corresponding to 0.1 ml. of titrant). These values have been considered to be constant over a range of chloride concentrations. In spectrophotometric work it may be assumed that instruments such as the Beckman Model DU or B will give readings reproducible within 1% transmittance or less, irrespective of dial reading. Based on these values, Figure 5 illustrates the variation of percentage error with concentration of chloride present in the unknown. The applicable experimental conditions were those outlined above (i.e., 100 ml. samples for the volumetric procedures, 2.5 ml. samples in a total of 10 ml. for the spectrophotometric procedure). The figure indicates that at low chloride concentrations a higher precision, expressed in terms of percentage error, can be expected from the spectrophotometric method. In the experimental studies it was found that deviations from the average in individual
measurements were well within the range defined by curve C. It can be inferred that the proposed spectrophotometric method is free from appreciable random deviations. The readings were reproducible within less than 1% transmittance. The percentage error reaches a minimum at 0.434 absorbancy unit which in this case corresponds to about 21 mg. per liter of chloride ion. At higher concentrations appropriate dilutions can be applied to obtain readings in the order of 0.434 absorbancy unit. According to Figure 5 at 17 mg. per liter of chloride the percentage error should be the same for procedure B and C (about 3%). Expressed in absolute amounts of chloride this uncertainty equals 50 µg. for procedure B, but only 1.2 µg. for procedure C.

An unambiguous evaluation of accuracy on the basis of this work does not seem to be possible. It appears from Tables III, V, and VI that at low chloride levels the Mohr method tends to give high results, if the titrant has been standardized against solutions of higher chloride content. This is consistent with the observation that the end-points become more distinct once an appreciable precipitate of silver chloride has formed. The reverse seems to hold for the mercurimetric method: At low chloride concentrations the results tend to be too low. This effect may be explained by the Law of Mass Action governing the dissociation of the mercury(II) chloride. At low chloride concentrations the values increased in the order of the procedures: Mercuric nitrate, spectrophotometric, Mohr.
Standardization of the titrants against varying amounts of chloride, comparable to a calibration curve, should lead to higher accuracies. In spectrophotometric work the accuracy will primarily depend on the quality of the calibration curve. In Table V and VI where the chloride concentrations were obtained from the same calibration curve, the results seem to be slightly low. Special care was taken in the preparation of the standard curve for the statistical runs (Table III); there the accuracy was practically ideal.

It is to be expected that the spectrophotometric method will be more sensitive towards colored contaminants. Treatment with aluminum hydroxide can be considered as adequate to eliminate such interferences in most cases.

It is felt that only in a few exceptional cases interference from other ions will render the spectrophotometric method inapplicable for the determination of chloride in water. Only sulfate ion, occasionally, may give rise to some difficulties. With respect to reliability, precision, and accuracy the proposed procedure compares advantageously with the standard titrimetric methods. Only a small volume of sample is required, and the operations involved are very simple.
CHAPTER FOUR

SPECTROPHOTOMETRIC DETERMINATION OF CHLORIDE IN AIR

Chloride is considered to be one of the common contaminants of air, yet the concentration limit above which it constitutes a health hazard greatly depends on the nature of the chemical combination in which it occurs in the atmosphere. Chloride ion as the anion of non-hydrolyzing salts, such as sodium chloride, is rarely ever referred to as a noxious or harmful constituent. Hydrogen chloride, on the other hand, or compounds which readily yield hydrochloric acid upon hydrolysis, because of their corrosive effect must be classified as industrial hazards. While the safety limit of chloride concentration, as established by the State Authorities of California, is around 15 mg. per cubic meter of air, the tolerable concentration of hydrogen chloride mist has been given as only 2 mg. per cubic meter.

For several years, therefore, air pollution studies included the quantitative estimation of small amounts of chloride. Yet no agreement has been reached so far in adopting one standard analytical method for this purpose. Following conventional procedures, the contaminant is trapped by bubbling air through distilled water or an
alkaline solution. Chloride is then quantitatively determined by titration after Mohr, Fajans, Volhard, or by means of mercury(II) nitrate. These more or less involved volumetric procedures can be replaced by a rapid and more sensitive nephelometric determination with silver nitrate.

Being aware of the advantages of spectrophotometric procedures, the author proposes a rapid quantitative estimation of chloride based upon the light absorption of the iron(III) chloro complex in perchloric acid at 350 μm. For reasons of simplicity and sensitivity, it seemed desirable to perform the sampling by bubbling air through the ready-made reagent, i.e., through a solution of iron perchlorate in perchloric acid. It is obvious that the hygroscopic properties of 8.5 M acid would extensively interfere with such a procedure. Table VII, columns 1 and 2 show at which concentrations of perchloric acid the vapor pressure of water above the solution is in equilibrium with the humidity in air. It appears that a reagent which contains 5 M perchloric acid represents a suitable compromise with respect to sensitivity as well as constancy of concentration when it is exposed to moist air. At 25° C air of 61% relative humidity is in equilibrium with 5 M acid. A relatively high concentration of iron perchlorate (0.1 M) was chosen to increase the sensitivity.
APPARATUS AND REAGENTS

A test tube, one inch in diameter and 7 inches long with a bulb-shaped expansion below the standard taper neck served as the sampling vessel. The air-inlet tube had a glass frit at its end and extended almost down to the bottom of the test tube, so that the frit was fully submerged when the vessel contained 10 ml. of solution.

In order to deliver accurately small quantities of hydrogen chloride gas into a current of air which subsequently was passed through the sampling vessel, a capillary gas-buret was connected with a gas dilution apparatus similar in design to the one described by Urone and Boggs. The capillary buret was 30 cm. long and contained a total volume of 0.4 ml. Hydrogen chloride gas was obtained from a Kipp generator charged with sodium chloride and concentrated sulfuric acid. Aspirated air was first passed through a wet-test meter and then dried and purified in a train of absorption tubes filled with silica gel, magnesium perchlorate and sodium hydroxide pellets.

The absorbancies of the solutions were measured in 1 cm. Corex cells by means of a Beckman Model DU spectrophotometer with a tungsten light source.

The standard sodium chloride solution used in this study contained 50.0 mg. of chloride per liter. Perchloric acid (5 M) was obtained by blending 550 ml. of 60% reagent grade acid with 450 ml. of distilled water. A standard
solution of iron(III) perchlorate was prepared as described in Chapter Two. By blending appropriate volumes of perchloric acid and iron perchlorate solution a reagent was prepared which contained 0.1 M iron(III) in 5 M acid.

EXPERIMENTS AND RESULTS

In analogy to the experiments described in Chapter Two the influence of acidity on absorbancy was studied. In the present case the solutions contained 0.1 M iron(III) perchlorate and 80 µg. of chloride per 10 ml. of solution. The results are presented in Figure 1, plot IA. Plot IB illustrates the increase of background absorbancy with iron concentration, measured with respect to distilled water. As can be deduced from a comparison with plot IIA in Figure 1, the effect of acidity upon absorbancy is less pronounced in the case of higher iron(III) concentration. The value for the expression \((1/A) \times (dA/dM)\)--where \(A\) designates absorbancy and \(M\) the molarity with respect to perchloric acid--at \(M = 5.0\) was found to be approximately equal to 0.2 in case IA and approximately 0.5 in case IIA. The extent of background absorption (IB) at \(M = 5\) was about equal to 0.200 absorbancy unit and was essentially unaffected by small variations in acidity. The significance of these results will be discussed in connection with the experimental error.

The sensitivity of the method as well as possible deviations from Beer-Lambert's Law were examined by means of
a calibration curve. Aliquots of the sodium chloride standard solution were transferred to 50 ml. beakers, evaporated to dryness, and dissolved in 10 ml. of iron perchlorate reagent (0.1 M iron(III) in 5 M acid). The amounts of chloride ranged between 25 and 125 µg. The absorbancies were measured at 350 mp against a blank. Fifty µg. of chloride in 10 ml. of reagent gave an absorbancy reading of 0.310 unit. The results conformed to Beer-Lambert's Law.

Next, the efficiency of the proposed method was tested under conditions similar to those encountered in actual air analysis. For this purpose chloride ion was "sampled" by means of the gas dilution apparatus. The capillary gas buret was filled with dry hydrogen chloride gas after care was taken to displace all the air by hydrogen chloride. All parts of the apparatus except the buret were then swept free from hydrogen chloride by aspirating with dry air. Two bubblers, each filled with 10 ml. of iron perchlorate reagent were connected in series with the gas dilution apparatus. One or 2 cubic feet of dry air were passed through the bubblers in a blank run to ascertain the absence of hydrogen chloride from the apparatus. In a test run the rate of flow of air was adjusted by means of a needle valve, and measured amounts of hydrogen chloride gas, ranging from 0.02 to 0.11 ml., were released from the capillary buret into the current of air. After each run the absorbancy of the solution in the first
bubbler was measured with respect to a blank. After completion of each 5 or 6 runs the amount of chloride in the second bubbler was determined in a like manner. By comparing the value found for the second bubbler with the total amount of chloride trapped in the first bubbler, the scrubbing efficiency was estimated and found to be better than 98%. The rate with which air was aspirated ranged between 6 and 8 cubic feet per hour. It may be noted that a sudden release of hydrogen chloride gas from the gas buret could not be avoided; yet practically all hydrogen chloride was trapped in the first bubbler. A plot of the amount of chloride measured vs. the amount of chloride as calculated from the volume of hydrogen chloride released, summarizes the results of these experiments (Fig. 6).

It was stated above that the iron perchlorate reagent at 25°C exhibits a vapor pressure of water which corresponds to that of air at 61% relative humidity. Because evaporation or condensation of water during the process of sampling will cause a change in concentration of the solution an error in the measurement will be introduced. This error may become appreciable if large samples of very dry or very moist air are taken. Table VII shows per cent. volume changes of the solution if one cubic foot of air is sampled at various relative humidities. These values were calculated from vapor pressure data of perchloric acid solutions as reported by Pearce and Nelson. The assumption was made that in the process of sampling
complete equilibration of air with water vapor takes place. Experiments, in which the loss of water was measured by weighings of the bubbler before and after sampling air of known humidity, showed a reasonable agreement with the volume changes listed in Table VII, and it is felt that the latter may serve as a basis for estimating the extent of possible errors.

The effect of light upon solutions as used in this procedure was evaluated by exposure to direct sunlight and to indirect dim lighting after known amounts of chloride had been added. Exposure to bright sunlight for 10 minutes caused a decrease in absorbancy of 7%, while the decrease due to dim light after 30 minutes amounted to less than 2%. If the solutions were well protected against light, no change in absorbancy was observed within 24 hours.

DISCUSSION AND CONCLUSION

Changes in volume of the reagent during sampling, as mentioned above, deserve some attention. The estimate of the resulting error may be illustrated by the following: Assume that the relative humidity amounts to 10%, and the air sample to one cubic foot. In the case of complete equilibration of air with water vapor in the process of sampling the volume decrease of the reagent will be 3.3% (Table VII, column 3). If the background absorption amounts to 0.200 absorbancy unit this will cause an increase of approximately 0.007 unit. Thus, the background
effect will only be appreciable in case of very low chloride levels and very large air samples. Perchloric acid is non-volatile, and a volume decrease of 3.3% is therefore associated with an increase in perchloric acid concentration (ΔM) of 0.17 M; and because it was found that \((1/A) \times (dA/dM) \times 100\) is equal to 20, where A stands for absorbancy of the chloro complex, the resulting error will amount to approximately \(0.17 \times 20 + 3.3 = 6.7\%\). It is to be expected, therefore, that only in rare cases a correction must be made for volume changes due to evaporation losses or absorption of water.

**Recommended Procedure**

Dissolve 60 g. of purified iron perchlorate in 450 ml. of distilled water. Add 550 ml. of 60% reagent grade perchloric acid. The resulting solution should contain approximately 0.1 mole of iron perchlorate and 5 moles of perchloric acid. Transfer exactly 10 ml. of this reagent to a bubbler of suitable dimensions, which, for protection from light, has been inserted in an opaque tube. Draw one cubic foot of air at a rate of approximately 0.1 cubic foot per minute through the solution. Measure the absorbancy at 350 mp with respect to iron perchlorate reagent as the blank. The amount of chloride present is read from a calibration curve. The latter is obtained as follows: Aliquots of sodium chloride standard solution are transferred to 50 ml. beakers and the water evaporated on
a hot plate. The amounts of chloride in the beakers should range between 15 and 150 µg. Transfer 10 ml. of iron perchlorate reagent to each beaker and swirl. Protect beakers from bright light. Measure the absorbancies of these standards with respect to a blank. The calibration has to be repeated every time a fresh reagent is prepared. If the reagent is to be kept over an extended period of time, occasional checks on the calibration curve are recommended.

Under the above conditions a chloride ion concentration in air of 1 mg. per cubic meter will give an absorbancy reading of approximately 0.180 if 1 cm. cells are employed.

The procedure proposed should prove itself useful in routine air analysis. Once the reagent has been prepared and the calibration curve set up, the operations only consist of pipetting the reagent into the bubbler, sampling, transferring the sample to the absorption cells, and measuring the absorbancy. The applicability of this method is hardly restricted by interferences and the sensitivity is higher than in most conventional analytical procedures. The error in the determination of chloride at concentrations of the order of 2 mg. per cubic meter of air should normally not exceed 5%. 
CHAPTER FIVE

THE STABILITY OF THE IRON(III) CHLORO COMPLEX

In the previous chapters several properties of the system chloride ion - ferric ion - perchloric acid have been established. No statement has been made about the nature of the complex or complexes responsible for the absorption band around 350 mp. Certain properties of the light-absorbing species--such as apparent extinction, temperature effects, sensitivity towards light--were found to be influenced by perchloric acid concentration. At first it was suspected that perchloric acid may function as a proton donor to some anionic complex, such as FeCl₄⁻, and in this manner account for the observed changes with acidity. Several experiments which were performed with strong nitric acid instead of perchloric acid gave some indication for a similar increase of extinction with acidity, although this effect was extensively obscured by the appearance of an intense absorption band in the same region of the spectrum upon interaction of ferric ion with strong nitric acid.

The assumption that FeCl₄⁻ or another anionic complex is formed--possibly a mixed chloro-perchlorato complex--meets with several difficulties, as will be shown in the following.

According to the concept developed by Pauling, 39
"ionic" bonds between central atom and ligand are ascribed to chloro complexes of iron(III), since their magnetic moment corresponds to that of the free ion.\(^{59}\) There is no evidence that a certain complex with more than one chlorine atom associated with the central atom excels with respect to stability, as this seems to be the case with certain "covalent" complexes where symmetry of the hybridized bonding orbitals may be the determining factor for the number of ligand atoms coordinated. The formation of the chloro complexes can be illustrated by the reaction sequence

\[
\begin{align*}
\text{Fe}^{+++} + \text{Cl}^- & \rightleftharpoons \text{FeCl}^{++} \\
\text{FeCl}^{++} + \text{Cl}^- & \rightleftharpoons \text{FeCl}_2^+ \\
\text{FeCl}_2^+ + \text{Cl}^- & \rightleftharpoons \text{FeCl}_3 \\
\text{FeCl}_3 + \text{Cl}^- & \rightleftharpoons \text{FeCl}_4^-.
\end{align*}
\]

Theoretical\(^{19}\) and experimental\(^{18,19}\) findings suggest that \(\text{FeCl}_4^-\), and not as formerly believed \(\text{FeCl}_{6}^{3-}\), represents the highest complex found in solution. It is then reasonable to assume that under the conditions discussed in the previous chapters, the lowest chloro complex, i.e., \(\text{FeCl}^{++}\), is the one most likely to be formed, since in every case the concentration of iron(III) largely exceeded that of chloride ion. Studies on the stability of iron(III) chloro complexes at low ionic strengths (<2), or in more concentrated hydrochloric acid in the case of the unstable \(\text{FeCl}_4^-\), strongly support this belief. Thus Rabinowitch and Stockmayer\(^{42}\) found the values 4.2, 1.3, 0.04 for \(K_1\), \(K_2\), \(K_3\) at an ionic strength of unity, where the stability constant \(K_n\) is defined
by \[ K_n = \frac{(\text{FeCl}_n^-)}{(\text{FeCl}_{n-1}^-)(\text{Cl})} \]. Gamlen and Jordan report the value of approximately 0.01 for \( K_4 \) at zero ionic strength. Therefore, if the ratio \( K_1/K_2 \) remains about constant irrespective of ionic strength, \( \text{FeCl}^{+ +} \) should be formed almost exclusively as long as the iron concentration remains much higher than the chloride concentration. \( K_1 \), according to Rabinowitch and Stockmayer, reaches a minimum of approximately 4.0 at an ionic strength (s) of 0.8, beyond which a steady increase with s is indicated. The observation that variations in iron(III) concentration had a greater effect upon absorbancy at low acidities suggested more extensive dissociation of the chloro complex, and hence an increase of \( K_1 \) with acidity. A study of stability constants at various acidities above 2 M therefore appeared necessary for an understanding of the observed phenomena. Spectrophotometric measurements were chosen as the most suitable means to determine the concentration of the absorbing species.

**Preliminary Considerations**

The subsequent determination of the apparent stability constants of the complex \( \text{FeCl}^{+ +} \) was based on the following considerations:

\[ A_t = A_r + E \times (\text{FeCl}^{+ +}) \]  
(Eq. 1)

where \( A_r \) stands for the residual (background) absorption and \( E \) for the molecular extinction coefficient.
After correction for the light absorption due to species other than FeCl$^{++}$ (subtraction of blank value), one obtains $A=E\times y$, where $y$ stands for the concentration of the complex.

Let $a$ be the total concentration of iron and $b$ the total concentration of chlorine in solution; then, since

$$K = \frac{(FeCl^{++})}{(Fe^{+++})(Cl^-)}$$

(Eq. 2)

(the subscript "l" of $K_1$ shall henceforth be omitted)

one may write

$$K = \frac{y}{(a-y)(b-y)}$$

(Eq. 3)

In order to simplify the expression for $K$, $a-y$ is tentatively treated as a constant $a'$. Then

$$y = \frac{a' b K}{1 + a' K}$$

(Eq. 4)

and

$$A = E \frac{a' b K}{1 + a' K}$$

(Eq. 5)

One may evaluate $E$ and $K$ in Eq. 5 by measuring $A$ as a function of $a'$. For this purpose one keeps $b$ constant and varies the concentration of iron(III), so that always $a > b$.

It is evident that the concentration of iron(III) has to be kept within reasonable limits, first, because the contribution from this ion to the total ionic strength of the solution should be negligible; further, the apparent stability constant $K$ has been expressed in terms of concentrations and not activities, which is justifiable only as long as the concentrations of the reacting species remain small. Eq. 5 shows then an inherent difficulty: In the case of a small $K$ the situation may arise that

$$a'K \ll 1$$

hence $E$ and $K$ in the numerator cannot be sepa-
rated. On the other hand, if $a'K \gg 1$, so that the denominator essentially equals $a'K$, $E$ can directly be determined from the limiting absorbancy $A_L$ as $A_L/b$. This situation corresponds to complete complexation of chloride ion.

Several methods may be employed for the evaluation of $E$ and $K$ in Eq. 5. Most suitable appeared to be a rearrangement of Eq. 5 so that

$$\frac{1}{A} = \frac{1}{K} \frac{1}{E} \cdot \frac{1}{a'} + \frac{1}{E}$$

(Eq. 6)

Thus, a linear relation between $1/A$ and $1/a'$ has been established, and the constants can readily be determined from slope $(m)$ and intercept $(c)$ of the straight line:

$$K = \frac{c}{m}, \quad E = \frac{1}{bc}.$$  

Preference was given to the graphical evaluation of $m$ and $c$ rather than to the more time-consuming calculation by the method of least squares. In addition, reliable values for $c$ and $m$ can only be established if correct weighting factors are assigned to $A$ and $a'$. An attempt was made to calculate such weighting factors from the theoretical error of the spectrophotometric measurements and by assuming a constant error in the volumetric transfer of the solutions. The actual significance of weighting factors calculated in this manner still appears debatable. The necessity of assigning weighting factors can be seen if one considers that small values of $A$ and $a'$ are subject to a rather large percentage error which is further magnified upon reciprocation. In a graphical representation of the experimental results such deviations can be estimated
more readily, and it is felt that in this manner more reliable results are obtained.

From previous experiments it was known that the wave length of maximum absorption changes with acidity, and no assumption was made with respect to the invariance of the molecular extinction coefficient of the complex at maximum absorbancy ($E_{\text{max}}$) with changes of acidity.

**Apparatus**

The measurements were performed with a thermostated Beckman Model DU spectrophotometer equipped with a tungsten lamp, and a Model DK-1 spectrophotometer for recording of absorption spectra. Matched 1 cm. quartz cells were used. The thermostat allowed a temperature control within ±0.5° C.

For comparison of vapor pressures a device was used as described by Baldes. Two Manganin - Advance thermocouples, bucking each other so that the Manganin wire was common to both couples, were connected with a sensitive galvanometer (0.005 µamp./mm.) via copper leads and a double-pole double-throw switch for reversal of polarity. At the junctions of the thermocouples the wires formed small loops about 25 mm. apart. The wires (diameters: Manganin 0.01, Advance 0.005 inch) were spot-welded at the junctions and then sprayed with a plastic insulating material. Finally the loops were coated with paraffin to prevent corrosion by perchloric acid. The
thermocouples were inserted in a water-tight cell. The principle of the method involved consists of measuring differences in temperature which arise from differences of vapor pressure (rates of evaporation or condensation) between an "unknown" and a reference solution in contact with the thermocouples. A difference in vapor pressure (water) of 0.02 mm.Hg caused a galvanometer deflection of the order of 1 mm. The unfavorable ratio of resistances between the galvanometer and the thermocouple (1000:1) somewhat impaired the efficiency of the device.

Solutions

Standard sodium chloride solutions contained 1000, 500, 200, and 100 p.p.m. of chloride, respectively.

Purified iron(III) perchlorate was dissolved in distilled water and the acidity of the solutions adjusted to 2 M with perchloric acid. The solutions were standardized by titration with dichromate. The final concentrations in the stock solutions were 0.522, 0.100, 0.0100, and 0.0050 M.

Perchloric acid (70%, Analytical Reagent, Merck) was stored in a closed-system buret. The acid was standardized against sodium hydroxide.

Sodium perchlorate solution (7.75 M) was prepared from hydrated reagent-grade sodium perchlorate. For the purpose of standardization aliquots were taken, the water first evaporated on a hot-plate, and the salt dried at
170° C, and then weighed.

Anhydrous magnesium perchlorate reagent was re-
crystallized from aqueous solution and was washed several
times with small portions of ether in order to remove
traces of an interfering contaminant (probably organic)
which gave a yellow color upon heating with perchloric acid.
The aqueous solution of the salt was standardized by
titration with ethylenediamine tetraacetate, eriochrome
black-T serving as the indicator. The molarity of the
magnesium perchlorate solution amounted to 2.78.

Sodium perchlorate and magnesium perchlorate were
obtained from G.F. Smith Chemical Company. Traces of
chloride ion were found in the sodium salt, while mag­
nesium perchlorate apparently was free from that
contaminant.

EXPERIMENTS AND RESULTS

In order to give further support to the assumption
that the complex in question corresponds to the formula
FeCl++, Job's method of continuous variation27 was applied.
Generally, the method is not applicable if more than one
species present exhibits those properties on which the
measurements are based.28 In the case considered here,
interferences were to be expected from the formation of
more than one colored species. Yet, if more than one
complex of iron contributes to the absorption band at
350 μm, irregularities should appear in the plot, and hence
such an interference should be recognizable.

The molecular ratio $M:X$ in a light-absorbing species $MX_n$ may be determined by varying $M$ and $X$ such that $(M) + (X) = \text{constant}$, and by measuring the absorbancy for each molar ratio chosen. Plotting absorbancy vs. $(X)/(M)$ gives a curve with a maximum at $(X)/(M) = n$, where $n$ designates the number of ligand atoms associated with $M$. The experiments were performed by measuring the absorbancy at 350 mp of 12 solutions whose chloride - iron(III) ratio varied between 0.118 and 3.35, the total concentration (chloride plus iron) being kept constant at $5.32 \times 10^{-4}$ M. The solutions were $8.5$ M with respect to perchloric acid. The maximum of the plot occurred at a ratio of 1:1 (Fig. 7) and no irregularities were observed in the descending branch between the abscissa values 1 and 4, which indicates that even at those molar ratios where chloride ion concentration exceeds that of iron(III), no appreciable quantities of higher complexes seem to be formed. This conclusion can be drawn because the higher chloro complexes of iron(III) also exhibit intense absorption bands at this wave length.\(^{19}\)

From preliminary experiments it was expected that at higher acid concentrations the values of $K$ should be much greater and therefore easier to determine, because the limiting absorbancy, $A_L$, could be approached more rapidly. Thus, the measurements were first performed on solutions which contained $9$ M perchloric acid, and the acidities
arranged in a decreasing order.

The calculated amount of perchloric acid was delivered into 10 ml. flasks protected against light by a black coating. Next, varying amounts of ferric perchlorate solution were added; the concentration of these solutions was adjusted in such a way that for a given chloride concentration the absorbancies of the samples did not give exceedingly high or low scale readings; likewise, the concentrations were chosen to give an approximately equal spacing of points in a plot of $1/A$ vs. $1/a'$. For one given set of measurements (at constant acidity) the chloride concentrations were kept constant, and the amount adapted to yield optimum scale readings. The flasks were filled to the mark, shaken, and covered with a bag of opaque paper and cooled to $25^\circ C$ in a constant temperature bath. A blank of the same composition, but without chloride, was prepared for every solution. Samples and blanks were transferred to the cells and placed in the thermostated cell compartment of the instrument. The absorbancies of both solutions were measured repeatedly with respect to distilled water until constant readings indicated thermal equilibrium. The readings for each set of solutions were taken at the wave length of maximum absorption. The values of the latter varied between 336 $\mu$ (2.5 M perchloric acid) and 352 $\mu$ (9.0 M acid). For comparison, absorbancies were also measured at a second wave length between 350 and 380 $\mu$, but only in the case
of samples with an acidity above 5 M. Each set of given acid concentration contained approximately 10 solutions.

K and E were calculated as follows: First, the blank value was subtracted from the absorbancy reading of the sample. A_L could roughly be estimated from the highest readings obtained at acid concentrations above 8 M. Thus the value of y (concentration of complex) could be estimated as approximately

\[ y = \frac{A}{A_L} b \]

(A = absorbancy of sample, b = total chloride concentration). Thus \( a' = a - y \) could be calculated with fair accuracy, since usually y was considerably smaller than a. Further corrections of the blank readings—the blanks contained a, the samples \( a - y \) moles of uncomplexed iron(III) per liter—were not found to be necessary. Next, \( 1/A \) was plotted against \( 1/a' \) and the best straight line drawn through the points. The precision was estimated by first drawing two "extreme" straight lines which still could be argued to represent correct results. The average of these extremes was then chosen as the best straight line, the deviations of the extremes as the experimental error. A certain arbitrariness inherent in this procedure cannot be denied. Having thus established slope and intercept one can calculate K and E for a given set.

In the next set the previously determined \( E_{\text{max}} \) was employed to estimate y and consequently a'. It was found that \( E_{\text{max}} \), within the limits of experimental error did not
vary with acid concentration. Yet the uncertainty—due to experimental error—reached considerable proportions at low acidities (small K). Values of $E_{\text{max}}$ determined at acidities above 6.0 M were averaged; this value of $2.91 \times 10^3$ henceforth was used to establish the intercept of all sets. This led to only insignificant corrections for the previously determined values of K for acidities above 6 M. The results are summarized in Table VIII and Figure 8.

The measurements at wave lengths of maximum absorbancy gave a very satisfactory linear relationship between $1/A$ and $1/a'$. Plots based on readings taken at other wave length showed a larger random error, and the linearity of the plots was less satisfactory than in the previous case.

Because of the remarkable effect of acid concentration on the stability of the chloro complex—K increased by three orders of magnitude between 2.5 and 9.0 M acid—, it was expected that other solvents than perchloric acid–water mixtures should lead to interesting results. Organic solvents such as methanol, ethanol, dioxane, acetone mixed with water or dilute perchloric acid could not be used, because upon addition of iron(III) perchlorate the solutions invariably turned yellow, probably due to solvolysis, and measurements in the near ultraviolet were meaningless for the purpose in mind. Perchlorates blended with perchloric acid seemed to remain as the only non-complexing, non-interfering solvents. Thus, mixtures containing 4.95 M acid and 0.775, 1.55, and 2.32 M sodium perchlorate were chosen
as the medium, and the stability constants determined by
the procedure outlined above. Finally, corresponding
determinations were made with blends of 4.95 M acid with
0.555 and 1.03 M magnesium perchlorate. The concentration
range of either salt was limited to these values because
larger quantities of salt could not be dissolved in perchloric
acid. Addition of salt likewise caused a slight
shift of the absorption band towards longer waves. From
the plot of log K vs. perchlorate concentration (Fig. 9) it
is evident that a separate curve exists for each medium.
Errors in the abscissa values should not exceed ±0.5% for
perchloric acid and sodium perchlorate blends, and
approximately ±0.7% in the case of magnesium perchlorate
mixtures. The smoothness of the curve in Figure 8
suggests a quite satisfactory precision of the results.
Figure 10 represents a plot of log K against the square
root of ionic strength, the latter being defined as \( \frac{1}{2} \sum m_i z_i^2 \)
where \( m_i \) stands for the molal concentration of each indi-
vidual ionic species and \( z_i \) for the corresponding ionic
charges. In order to calculate molalities from molarities,
the densities of the solution had to be known. These were
partly obtained from the literature; the densities of the
blends were determined by weighing accurately pipetted
volumes of solution. It is understandable that plots of
log K against molarities had little significance if the
branching of the curves should be explained. Likewise, a
plot against \( \sqrt{s} \) at such high concentrations can hardly be
considered as amenable to theoretical interpretations. It was hoped that a new aspect could be gained by establishing \( \log K \) as a function of vapor pressure of water above the solutions.

Perchloric acid as well as perchlorates are non-volatile. Therefore, the method of Baldis was quite applicable for the determination of vapor pressures. Nine perchloric acid standards, ranging in concentration from 5.00 to 7.00 M, were prepared. About 2 ml. of the solution whose vapor pressure was to be determined were used to moisten the bottom and walls of the cell. One drop of the unknown was placed in one loop of the thermocouple, and a drop of perchloric acid standard in the other. The cell was closed and thermostated at \( 25 \pm 0.1^\circ C \) and the galvanometer deflection in either direction recorded after 10 minutes. The procedure was repeated with a drop of the next perchloric acid standard, and so on, until the unknown was found to correspond to some concentration between two standards. The relationship between galvanometer deflections and differences in vapor pressure was found to be approximately linear over a narrow range. Two freshly prepared standards which differed in molarity by 0.10 were chosen to bracket the unknown in a final measurement. The procedure was repeated after a reversal of thermocouples. The reliability of the method was established by means of duplicates. The sensitivity appeared to be quite adequate for the purpose in mind. The results were expressed in
terms of vapor pressures of water (mm. Hg) as determined by Pearce and Nelson\textsuperscript{40} for pure aqueous solutions of perchloric acid. The plot of log K vs. vapor pressure of water (Fig. 11) reveals a significant change with respect to the sodium perchlorate mixtures (B). The log K values are shifted slightly above those of pure perchloric acid (A), while the magnesium perchlorate curve has undergone only a minor shift towards curve A.

Of further interest appeared to be a comparison of the thermodynamic data, $\Delta F^0$, $\Delta H^0$, $\Delta S^0$, determined at two different acid concentrations. For this purpose the stability constants of the iron(III) chloro complex were evaluated for 3.0 and 8.5 M acid over a temperature range from 25 to 45° C. The constants were determined by the procedure described above. The exact control of temperature presented some difficulty, and an error of $\pm 0.3$ to $\pm 0.5° C$ is likely. $\Delta F^0$, the change in standard free energy, was calculated from the relation $\Delta F^0 = -RT\ln K$, and $\Delta H^0$, the standard enthalpy change, could be evaluated from a plot of log K vs. $1/T$ (Fig. 12). According to the Gibbs-Helmholtz equation

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H^0}{R},$$

(Eq. 7)

so that $-\frac{\Delta H^0}{2.3R}$ equals the slope of the tangent drawn to the curve at a certain reciprocal absolute temperature. $\Delta S^0$, the standard entropy change, was calculated from $\Delta F^0 = \Delta H^0 - T \Delta S^0$. Obtained were the following results:
<table>
<thead>
<tr>
<th>Acidity (M)</th>
<th>$\Delta F^\circ$ (Kcal./mole)</th>
<th>$\Delta H^\circ$ (Kcal./mole)</th>
<th>$\Delta S^\circ$ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>-2.4</td>
<td>3.8</td>
<td>21</td>
</tr>
<tr>
<td>8.5</td>
<td>-4.74</td>
<td>-2.3</td>
<td>8.2</td>
</tr>
</tbody>
</table>

The fact that these values are not the same in both cases deserves some attention. It was pointed out at the beginning that $K$ does not represent a true thermodynamic equilibrium constant for the reaction

$$Fe^{+++} + Cl^- \rightleftharpoons FeCl^{++},$$

but rather an apparent equilibrium constant. A complete representation of the reaction must also account for the respective reaction medium. The influence of acid concentration, as reflected in the discrepancy of the thermodynamic constants, will be discussed in the next section.

Finally, Figure 13 shows a spectrum of FeCl++ from 500 to 225 m\(\mu\) in 9.0 M perchloric acid, recorded with respect to a blank of ferric perchlorate in acid of the same concentration. The quantity of ferric perchlorate in the blank was chosen to compensate for the amount of non-complexed iron in the sample containing chloride. The broken line represents the absorption spectrum of iron(III) perchlorate in 10 M perchloric acid. The spectra agree qualitatively with those reported in the literature.
DISCUSSION OF RESULTS

From the evidence available it can be concluded that the colored species, which was made the subject of this investigation, corresponds to the formula FeCl\(^{++}\). With reference to the information available from literature, the monochloro complex was postulated as the most likely one. Some proof, although not quite reliable, was furnished by Job's method of continuous variation. The linear relation between \(1/A\) and \(1/a'\), finally, gives the strongest support in favor of the correctness of this formula. For any composition of the complex one may write the stability constant as

\[
K_n = \frac{(FeCl_n)}{(Fe)(Cl)_n^n} \quad \text{or} \quad K_n = \frac{y}{a'(k-y)^n} \quad \text{(Eq. 8, 9)}
\]

Solving for \(y\), one obtains a linear relationship only if \(n=1\). Further, it can be inferred that only one chloro complex accounted for the observed absorption band.

The increase of stability with acid concentration then explains the apparently higher extinction and the less pronounced influences of changes in ferric ion concentration and acidity in Procedure 1 of Chapter Two: Under these conditions practically all chloride ion present has been complexed. A change in stability, e.g., from \(K=3000\) to \(K=2000\) would only cause a relatively small percentage error in the spectrophotometric reading. The maximum of absorbancy at 8.5 M acid in Figure 1, plot IIA, is only fortuitous. It is due to a shift of the absorption band.
towards longer waves with increasing acid concentration, i.e., only the value for 8.5 M acid was measured at the absorption peak.

Rabinowitch\textsuperscript{41, 42} and Stockmayer,\textsuperscript{42} in a criticism of v. Kiss\textsuperscript{29} extinction curves of hydrated iron(III), point out that even in 2.55 M perchloric acid a certain amount of the hydroxo complex FeOH contributes to the extinction. The absorption spectrum of 0.1 M iron(III) perchlorate in 2.5 M perchloric acid, as determined in the present investigation (Fig. 4, curve 4), differs somewhat from the one obtained by v. Kiss and coworkers. From the slight inflexion of the curve at 350 mp one may suspect the presence of small amounts of another species, either FeOH\textsuperscript{++} or FeCl\textsuperscript{++}, the latter due to trace impurities of chloride present in the iron(III) perchlorate. This inflexion was observed in several batches of purified reagent, but seemingly an increase in acidity from 2.0 to 5.5 M had no influence, except that the entire band was slightly shifted towards longer waves. Such a behavior makes a contribution from FeOH\textsuperscript{++} appear unlikely, since the absorption peak of the hydroxo complex lies further to the red end of the spectrum than the band of the hydrated iron(III).

If one extrapolates the log K curve in Figure 8 to an abscissa value of 2 M acid one obtains K approximately equal to 3.3. Olerup\textsuperscript{37} reported K=5.7 at 20\textdegree{} C in 2 M perchloric acid; referred to 25\textdegree{} C this value would still
be somewhat higher. Rabinowitch and Stockmayer, in a range from 0 to 2 ionic strength (s), represent their results by the formula

$$\log K = 1.51 - \frac{3\sqrt{s}}{1 + 3\sqrt{s}} + 0.295s$$  \hspace{1cm} (Eq. 10)

At s equal 2.0 K=5.6, in fair agreement with Olerup's result, but appreciably higher than the extrapolated value obtained by the present author. Rabinowitch and Stockmayer measured absorbancies of more concentrated solutions around 400 mp; they determined the constants K and E from a function \(y=ax/(1+bx)\) which gave the best agreement with their experimental points in a plot of absorbancy vs. iron(III) concentration. It was mentioned above that without a previous knowledge of the molecular extinction coefficient the experimental error in the case of a small K can become quite extensive; this, in some respect, may explain the disagreement of results. Furthermore, these authors also assumed E—which refers to a wave length far remote from that of maximum absorption—to be invariant with ionic strength. In view of the shift of absorption bands with acidity as well as ionic strength in general, such an assumption is hardly justifiable, because only a minute displacement of the band will cause noticeable absorbancy changes at all wave lengths where the absorption curve exhibits a large slope. This fact may also partly account for the discrepancy between the results. Bray and Hershey, at an ionic strength below 1, obtained slightly lower values, Bent and French, at s=0.65,
reported $K = 0.78$, compared with approximately 4.0 found by Rabinowitch and Stockmayer. The reliability of this exceedingly low value by Bent and French appears to be questionable.\(^{19, 42}\) From measurements of electromotive force Brosset\(^{8}\) arrived at $K = 2.27$, lower than any value which would correspond to Eq. 10. Olerup\(^{37}\) determined $K$ spectrophotometrically at 366 mp; the result was confirmed by electrometric measurements. Details on the method applied are not known to the author of this dissertation. Gamlen and Jordan\(^{19}\) in a graph cite molecular extinction coefficients of FeCl\(^{1+}\) reported by Olerup\(^{37}\). There, $E_{\text{max}}$ amounts to approximately 1400, compared to 2910 found in this investigation. This discrepancy cannot be explained without a more detailed knowledge of Olerup's work. It may be noted, however, that the product $K \times E_{\text{max}}$ seems to give a much better agreement.

In this place an attempt shall be made to offer an explanation for the remarkable influence of acidity upon the stability of the chloro complex.

The apparent stability constant was written as

$$K = \frac{[\text{FeCl}^{1+}]}{[\text{Fe}^{1++}][\text{Cl}^{-}]}.$$  

A theoretical constant may be expressed as

$$K_0 = \frac{[\text{FeCl}^{1+}]}{[\text{Fe}^{1++}][\text{Cl}^{-}]} \frac{f_c}{f_a \cdot f_b}$$  \hspace{1cm} (Eq. 11)

where $f_a$, $f_b$, $f_c$ stand for the respective activity coefficients. Hence

$$K = K_0 \frac{f_a \cdot f_b}{f_c}$$  \hspace{1cm} (Eq. 12)

In the state of reference $K = K_0$. Addition of large quantities of electrolyte, among other effects, will cause a
partial removal of the hydration sphere of a certain species. Strong perchloric acid, known as a dehydrating agent, can be expected to act in this very manner. Partial dehydration of ferric ion, particularly if also the inner hydration sphere is affected, should cause a pronounced rise of activity in the reaction with chloride ion. Chloride ion, in order to react, has to penetrate the outer hydration sphere of the ferric ion, and then occupy one of the six sites of the inner sphere which is normally filled with water molecules held by the central atom by an ion-dipole bond. Similarly, chloride ion itself has first to break up its own hydration sphere. Thus, it is reasonable to assume that dehydration will cause a change in \( f_b \) in the same sense as in \( f_a \), and the apparent stability constant will increase with acidity or ionic strength as soon as these effects become predominant. In order to have a more reasonable basis for comparison, the activity of water was chosen as a variable rather than perchlorate ion concentration, because a direct influence of the latter could hardly lead to an increase in stability of the chloro complex.

Tentatively, each activity coefficient may be expressed as the product of two contributing factors, one of which is to be specific to activity of water (\( f'' \)).

Thus

\[
K = K_o \frac{f_a}{f_c} \frac{f''}{f_c} \frac{f_a}{f_c} \frac{f'}{f_c} \tag{Eq. 13}
\]

or

\[
\log K = \log K_o + \log \frac{f_a}{f_c} + \log \frac{f''}{f_c} + \log \frac{f_a}{f_c} \frac{f'}{f_c}
\]
Activities are proportional to fugacities, and the latter in this case practically equal to vapor pressures, so that the vapor pressure of water above the solution is a true measure for the activity of water in the respective medium. All other influences disregarded, the plot of log $K$ vs. the vapor pressure of water for perchloric acid and the salt mixtures should yield only one curve. This, however, could not be verified.

The disagreement should therefore arise from direct effects of other ions, specific for each medium. Interaction between ionic species of opposite sign deserves special attention. A perhaps not unreasonable assumption is that perchlorate ion will exert about the same direct influence on $f'_a$ and $f'_c$. All that remains then is the interaction between chloride ion and the cation which is characteristic for the medium. Numerical values for the activity coefficients of chloride ion (or hydrochloric acid) in fairly concentrated solutions of acids other than hydrochloric acid, and the corresponding sodium and magnesium salts, upon substitution in Eq. 13 should reduce the three curves in Figure 11 to a single one. Unfortunately no such data are available. It may be noted that $f'_b$ only refers to that portion of the activity coefficient which is directly related to the cation concentration, while normally activity coefficients will also include the factor which accounts for the influence of hydration. An approximate separation of these two factors may be possible if activities of chloride
ion as well as vapor pressures of water were known for several ionic media, such as perchlorates, sulfates, nitrates. An extension of this work to comprise, e.g., lithium, calcium, and aluminum perchlorates, may be worth while, particularly, if the accuracy of the determinations could be increased. The order suggested by Figure 11, i.e., log K (Na) > log K (H) > log K (Mg) cannot be taken as a basis for a qualitative explanation of cation influences, because the contribution from $f_0$ does not appear as a function of molality but refers to activities of water, a scale which is not directly related to cation concentration.

It is safe to assume that the reaction between ferric ion and chloride, in a very simplified form only, will be represented by the equation

$$Fe^{+++} + Cl^- \rightarrow FeCl^{++}.$$ 

It appears to be more appropriate to include also other processes to account for the complete reaction, such as

1. $$Fe(H_2O)_6^{+++} \rightarrow Fe(H_2O)_5^{+++} + H_2O$$
2. $$Cl^- (aq.) \rightarrow Cl^- (dehydrated)$$
3. $$Fe(H_2O)_5^{+++} + Cl^- (deh.) \rightarrow FeCl(H_2O)_5^{++}$$

The first two steps can be expected to be endothermic, while step (3) is exothermic. $\Delta H^0$, determined for the reaction in 3 M perchloric acid, then represents the algebraic sum of the individual enthalpy changes, and hence it is not surprising that a positive value is obtained. It has been assumed that in 8.5 M acid at least partial dehydration of the reacting species occurs. Accordingly, contributions to $\Delta H^0$ from the
first two steps have lost their preponderance, and $\Delta H^0$ is negative. A similar explanation will also account for the changes in entropy. Charged particles (ions) will tend to align the polar solvent molecules and thus establish a more or less ordered arrangement throughout the medium. The extent of alignment will depend on the total number of charges involved, irrespective of sign. In the reaction of ferric ion with chloride the total number of charges is reduced from 4 to 2, which leads to a less rigid alignment of water molecules. Consequently, $\Delta S^0$ will be positive for this reaction. The aligning power of the reacting species is suppressed by the action of perchloric acid, the extent of this effect depending on the concentration of the acid. Hence a smaller positive $\Delta S^0$ should result at 8.5 M acid, a prediction vindicated by the experimental results. Consistent with this interpretation are the values obtained by Rabinowitch and Stockmayer\textsuperscript{42} for zero ionic strength, who calculated $\Delta H^0 = 8.5$ Kcal./mole and $\Delta S^0 = 35$ entropy units.

In the opinion of the author the findings of this investigation invite some doubt as to the existence of iron(III) perchlorato complexes. Sutton,\textsuperscript{51} who estimated the stability constant of the complex $\text{FeClO}_4^{++}$ as approximately 0.5, determined this value spectrophotometrically at perchloric acid concentrations between 2 and 7 M. The basis for this determination seems to be the shift in the absorption band attributed to ferric ion as a function of
perchloric acid concentration. An alternative explanation for this observation may be given by interpreting the spectral changes as being due to the degree of dehydration of ferric ion, instead of association with perchlorate (Fig. 14). A quite analogous shift of the absorption band occurred in the case of the chloro complexes. Two points in favor of the dehydration concept should be recalled: (1) The chloro complex exhibits an unusual stability at high concentrations of perchloric acid. Such an effect is to be expected from a partial dehydration of the central atom. Consequently, chloride ions more readily find access to the ferric ion, and the equilibrium of the reaction $\text{Fe}^{+++} + \text{Cl}^- \rightleftharpoons \text{FeCl}^{++}$ is shifted to the right. On the other hand, formation of perchlorato complexes, even of low stability, can be expected to exert an opposing effect on this reaction, i.e., perchlorate ion should to some extent "mask" the ferric ion, in analogy to the action of water at low acidities. (2) A greatly reduced solubility of iron perchlorate in 70% perchloric acid was observed. Addition of water greatly enhanced the solubility. The existence of complex ions of the formula $\text{FeClO}_4^{++}$ can hardly be reconciled with this observation. Yet, such a behavior can be expected if one assumes removal of the hydration sphere. More recently Sykes\textsuperscript{53} has published a paper in which he claims that even at a concentration of 0.15 M perchloric acid, 30% of the ferric ions are associated with perchlorate ions. Unfortunately, only an abstract of Sykes' publication
which does not give any details on the kind of evidence presented is available to the author of this dissertation.
Throughout the experimental work with the iron(III) chloro complex precautions had to be taken to protect the solutions from bright light. Exposure to intense light, especially to sunlight, had a marked effect on the absorbancy of the solution, particularly at high acidities, noticeable by an apparent disappearance of the monochloro complex. This phenomenon of sensitivity towards light seems to be common to most complexes of iron(III). Rabinowitch,\textsuperscript{41} in 1942, postulated such a behavior for complexes of transition elements in general, under the condition that the bond between the ligand and the central atom is "ionic". Absorption of light by complexes may essentially be attributed to electron transitions in the central atom, the bond between ligand and central atom, and in the ligand itself. The first type, a forbidden d - d excitation characteristic for most metals of the transition series, gives rise to very weak bands in the visible or the near ultraviolet region of the spectrum, the coefficients of maximum molecular extinction being smaller than 100. The weak absorption band of ferric ion around 400 μm (Fig. 4, curve 4) can be attributed to an electron transition in the 3d orbitals. Of special concern in
According to Rabinowitch\textsuperscript{41} electron transitions between orbitals of the ligand and the central atom give rise to very intense characteristic absorption bands of complexes, primarily observed in the ultraviolet. According to theory, and as verified by experiments in more recent years, such an electron transfer from the ligand to the central atom should, in general, result in a reduction of the latter while the ligand is transformed into a free radical. A dark reverse reaction with recovery of the original complex is assumed, but dissociation of the primary products of the electron transfer may occur, followed by further reactions, such as reversal of the preceding process, or secondary reactions depending on the nature of other species present in solution. The following scheme, proposed by Evans and Uri\textsuperscript{15} for the photolytic dissociation of FeOH\textsuperscript{2+}, illustrates the processes involved:

\[
\begin{align*}
\text{Excitation and primary dark back reaction} & \\
\text{Separation of primary products} & \\
\text{Secondary dark back reaction} & \\
\end{align*}
\]

Frequently the electron transfer mechanism is employed for initiating polymerization of an organic monomer M:

\[
\text{Fe}^{2+}\text{OH} + \text{M} \rightarrow \text{Fe}^{2+} + \text{HO-M}^{-}
\]

Analogous reactions have been reported by several authors. Evans and Uri\textsuperscript{15} mention photosensitized polymerizations in the presence of FeCl\textsuperscript{2+}, FeF\textsubscript{3}, FeC\textsubscript{2}O\textsubscript{4}\textsuperscript{2+}; FeBr\textsuperscript{2+} and FeSCN\textsuperscript{2+}.
likewise undergo dissociation in the above sense. Similar reactions which involve ceric ion\textsuperscript{16, 23, 52, 58} have been studied. In certain respects the mechanism of the photodissociation is not quite clear. Cobalt(III), e.g., in solution displays two fairly weak bands at 605 and 426 μm, and an intense band at 250 μm, the latter being identified as an electron transfer band. Yet, illumination with light of 426 μm causes photoreduction to Co(II).\textsuperscript{5} It seems that in this case a primary excitation of a d-electron of cobalt is instrumental in the electron transfer process which leads to subsequent reduction of the ion. Williams\textsuperscript{60} infers that primary excitation of d-electrons may be involved in the normal electron transfer process, which complicates the original picture of direct excitation of the transfer electron by a light quantum of corresponding energy.

Until recently, it was believed that photoreduction of iron(III) could only be observed if compounds participate, which either act as reducing agents or undergo free-radical initiated polymerizations. Good and Purdon,\textsuperscript{21} however, have conclusively shown that hydroxo and possibly chloro complexes of iron(III) in pure aqueous solution undergo such a photolytic dissociation, while similar reactions previously were attributed to the presence of contaminants in water. The same authors\textsuperscript{22} in an extension of their studies on photoreduction of iron(III) observed the formation of oxygen upon exposure to light from a mercury arc,
and the assumption that hydroxo complexes are the active species was supported by the finding, that addition of chloride ion had a depressing effect on the evolution of oxygen. It was also found that unirradiated solutions of iron(III) perchlorate could not be completely degassed, a fact which was interpreted as the formation of oxygen as a result of thermal decomposition of iron perchlorate, analogous to the photolytic process. Evolution of oxygen has also been observed by Dain and Kachan\textsuperscript{12} in a study of acidic ferric perchlorate solutions irradiated with ultraviolet light.

With respect to the conclusions drawn by these investigators, the processes involved in the action of light on the system concerned in this study may be formulated as

\[
\begin{align*}
\text{Fe}^{3+} + \text{Cl}^- & \xrightleftharpoons{\text{hv}} \text{Fe}^{2+} + \text{Cl}^- \\
\text{FeCl}^{2+} & \xrightarrow{\text{?}} \text{Fe}^{2+} + \text{Cl}^- \\
2 \text{Cl}^- + \text{H}_2\text{O} & \rightarrow \text{HCl} + \text{HOCl} \\
2 \text{HOCl} & \rightarrow 2 \text{HCl} + \text{O}_2.
\end{align*}
\]

The first two steps agree with a scheme proposed by Rabino-witch\textsuperscript{11} in a theoretical discussion of electron transfer phenomena.

In the following a few experiments will be discussed which show that the above scheme offers a reasonable explanation for the observed phenomena.

A problem arises when an attempt is made to compare the photochemical behavior of FeCl\textsuperscript{2+} in solutions of
different acidities, because the relative concentrations of
the species involved in the equilibrium reaction depend on
the respective medium. A constant concentration of the
chloro complex was chosen as the basis for the experiments
whose results are summarized in Figure 15. The concen-
tration of uncomplexed iron(III) in equilibrium with the
complex was maintained twice as high as the total amount
of chloride present in solution. Twenty ml. of the sample,
containing $2.4 \times 10^{-4}$ moles of FeCl$^{++}$ per liter, were trans-
ferred to a Pyrex cell surrounded by a cooling jacket;
the cell was located in one focal point of an elliptical
reflector with magnesium oxide coating; the light source,
a low-pressure mercury arc, was in the second focal point.
The absorbancy of the sample was measured by means of a
Beckman Model DU spectrophotometer at the wave length of
maximum absorption of the complex. Readings were taken
before irradiation, and after an exposure time of 50, 600,
1500, and 3600 seconds. For this purpose a small sample
was withdrawn from the reaction cell. It was found neces-
sary to take several measurements for each sample and to
extrapolate the absorbancies to zero time, i.e., the time
of withdrawal from the cell. At a specified time an ali-
quot of 0.2 ml. was accurately transferred to a 5 ml. flask
containing acetate buffer and 2 ml. of 0.2% $\alpha,\alpha'$-dipyridyl.
This solution was brought to volume with a few drops of
distilled water. The absorbancy of the Fe(II) $\alpha,\alpha'$-di-
pyridyl complex was measured at 522 mp in a Beckman Model
B spectrophotometer, and the readings were compared with a calibration curve. The readings had to be taken within 10 minutes after transfer of the 0.2 ml. aliquot, because the concentration of iron(II), in the presence of α,α'-dipyridyl, increased with time, more rapidly if the solutions were not protected against light. The following table shows the quantities of iron involved in experiments with 6 solutions:

<table>
<thead>
<tr>
<th>Acidity M</th>
<th>Total conc. M x 10^-5</th>
<th>Fe(II) found after 1 hour of irrad. M x 10^-5</th>
<th>Fe(II), in% of total iron concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>960</td>
<td>8.8</td>
<td>0.92</td>
</tr>
<tr>
<td>5</td>
<td>464</td>
<td>19</td>
<td>4.1</td>
</tr>
<tr>
<td>6</td>
<td>276</td>
<td>20</td>
<td>7.2</td>
</tr>
<tr>
<td>7</td>
<td>172</td>
<td>33</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>112</td>
<td>35</td>
<td>31</td>
</tr>
<tr>
<td>9</td>
<td>85</td>
<td>29</td>
<td>34</td>
</tr>
</tbody>
</table>

Although not too great an accuracy can be claimed for the determination of iron(II)—the experimental error may be of the order of ±5 to 10%—a rise of Fe(II) concentration with acidity is evident. The influence of light on the iron(III) chloro complex is summarized in Figure 15, where, for the respective acidities and time of irradiation, the amounts of this complex present in solution are expressed in per cent of the original FeCl^{++} concentration.

The most obvious phenomenon in this study was the rapid disappearance of the species FeCl^{++} when the strongly acidic solution was exposed to the light of the mercury arc. A comparison of the spectral band attributed to FeCl^{++} before and after irradiation, and after extended storage of the irradiated sample in the dark, only revealed a change of intensity but no qualitative differences. The con-
centrations of Fe(II) increased with acidity of the medium as well as with exposure to light. The complex FeCl$^{++}$ in solutions whose absorbancy had decreased to a fraction of the original in the course of irradiation, seemed to be partly recovered after extended storage in the dark; under the same condition the concentration of Fe(II) was found to decrease slightly with time. However, the original concentration of FeCl$^{++}$ could not be attained, even if the solutions were kept in darkness for several days. Increase of absorbancy, interpreted as recovery of FeCl$^{++}$, was rapid during the first minutes after irradiation was discontinued, but gradually leveled off. Thus, in the case of a solution 9 M with respect to perchloric acid, the absorbancy had dropped from 0.695 to 0.023 in the course of irradiation for one hour. After 5 minutes of darkness the absorbancy had risen to 0.042, after 11 hours to 0.250 unit. With respect to the above reaction scheme, such a behavior is to be expected. Calculation showed that the amount of iron(III) reduced to iron(II) did not suffice to account for the diminution of FeCl$^{++}$ concentration, and it can be concluded that the chloro complex actually participates in the photodissociation; the alternative assumption that perhaps Fe(III) in an interaction with water molecules constitutes the only photosensitive species cannot be reconciled with these experimental findings.

The experiments were limited to analysis with respect to the amount of FeCl$^{++}$ left and Fe(II) formed in the pro-
cess of irradiation. To verify fully the proposed mechanism the irradiation experiments must be extended to solutions of various iron(III) and chloride concentrations; likewise, a quantitative determination of oxygen would be necessary. In particular it remains to be explained why an increase of acidity has such a remarkable influence on the photostability of FeCl\textsuperscript{2+}. One factor contributing to this phenomenon is the considerably enhanced dissociation of the chloro complex at low acidities; here, disappearance of a certain amount of Fe(III) and Cl\textsuperscript{-}, in the sense of 
\[
\text{Fe}^{3+} \text{Cl}^- \xrightarrow{\lambda} \text{Fe}^{2+} + \text{Cl}^-
\]
involves a much smaller percentage change in the total Cl\textsuperscript{-} and Fe(III) concentration (at a given concentration of FeCl\textsuperscript{2+}) than would be the case if practically all Fe(III) and chloride had been associated. Yet, by itself, this explanation is insufficient. Other differences must exist in order to account for the observed facts. The increase of Fe(II) concentration with acidity upon irradiation for a given length of time suggests that the backward reaction, by which a recovery of the original species FeCl\textsuperscript{2+} takes place, is favored at low acidities. With reference to the experimental evidence it cannot be decided whether at low acidities this implies the reversal of the electron transfer, i.e., Fe\textsuperscript{3+}Cl \rightarrow Fe\textsuperscript{2+}Cl\textsuperscript{-}, to be favored, or whether secondary reactions, such as
\[
2 \text{Cl} + \text{H}_2\text{O} \rightarrow 2 \text{Cl}^- + 2 \text{H} + \frac{1}{2} \text{O}_2,
\]
account for the recovery of Fe(III) and Cl\textsuperscript{-}. Necessarily,
these secondary reverse processes must also include Fe^{++} \rightarrow Fe^{+++} \text{; otherwise, the concentration of } Fe(II) \text{ would rise rapidly and lead to a gradual disappearance of } FeCl^{++}, two facts in apparent disagreement with experimental evidence.
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## APPENDIX

### Table I

**Interferences**

<table>
<thead>
<tr>
<th>Species</th>
<th>Interference</th>
<th>Procedure 1</th>
<th>Interference</th>
<th>Procedure 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₄⁻</td>
<td>s.(p) 200(30)</td>
<td>m.(p) 16(4)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>n.(p) 300</td>
<td>n.(p) 2500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃COO⁻</td>
<td>none</td>
<td>n.(p) 4000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNS⁻</td>
<td>decomposes</td>
<td>h.(p) 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br⁻</td>
<td>m.(p) 11; corr.</td>
<td>m.(p) 4d</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I⁻</td>
<td>s.(p) 700; ppt. above 200 mg./l.</td>
<td>m.(p) 20; ppt. above 200 mg./l.</td>
<td>s.(n) 40</td>
<td>s.(p) 20</td>
</tr>
<tr>
<td>F⁻</td>
<td>n.(n) 400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>n.(n) 850</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg(II)</td>
<td>h.(n) must be absent</td>
<td>h.(n) must be absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(III)</td>
<td>n.(p) 200</td>
<td>n.(p) (&gt;1000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(II)</td>
<td>n.(p) 300</td>
<td>n.(p) 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>n.(n) 500</td>
<td>n.(n) 600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>n.(p) 600</td>
<td>n.(p) 300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(II)</td>
<td>n.(p) 1000</td>
<td>none</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>n.(n) (&gt;1000)</td>
<td>n.(n) 200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu(II)</td>
<td>n.(n) (&gt;1000)</td>
<td>n.(n) (&gt;1000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>ppt. above 300 mg./l.</td>
<td>ppt. above 400 mg./l.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figures in brackets refer to mg./l. of interfering ion giving the same absorbancy as 1 mg./l. of chloride. Figures in parenthesis refer to mg./l. of interfering ion causing a 3% error in the chloride value (these values were established at chloride levels of 5 and 8 mg./l. for procedures 1 and 2 respectively).

Extent of interference: n-negligible, s-slight, m-moderate, h-heavy; (p) indicates a positive, (n) a negative deviation.
Table II

Interferences from Bromide, Corrections

<table>
<thead>
<tr>
<th>Conc. of chloride mg./l.</th>
<th>Conc. of bromide mg./l.</th>
<th>Absorbancies measured at 353 μm 420 μm</th>
<th>Absorbancies calc. theor. 353 μm</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>16</td>
<td>0.332 0.434</td>
<td>0.289 0.213</td>
<td>-1.9</td>
</tr>
<tr>
<td>2.5</td>
<td>16</td>
<td>0.355 0.420</td>
<td>0.245 0.213</td>
<td>+15</td>
</tr>
<tr>
<td>2.5</td>
<td>40</td>
<td>0.504 1.095</td>
<td>0.207 0.213</td>
<td>-2.8</td>
</tr>
<tr>
<td>2.5</td>
<td>40</td>
<td>0.498 1.11</td>
<td>0.195 0.213</td>
<td>-8.5</td>
</tr>
<tr>
<td>5.0</td>
<td>8</td>
<td>0.475 0.220</td>
<td>0.426 0.427</td>
<td>-0.2</td>
</tr>
<tr>
<td>5.0</td>
<td>16</td>
<td>0.541 0.438</td>
<td>0.432 0.427</td>
<td>+1.2</td>
</tr>
<tr>
<td>5.0</td>
<td>32</td>
<td>0.649 0.838</td>
<td>0.427 0.427</td>
<td>0.0</td>
</tr>
<tr>
<td>5.0</td>
<td>40</td>
<td>0.722 1.10</td>
<td>0.428 0.427</td>
<td>+0.2</td>
</tr>
<tr>
<td>5.0</td>
<td>40</td>
<td>0.710 1.10</td>
<td>0.416 0.427</td>
<td>+2.6</td>
</tr>
</tbody>
</table>

The above values were obtained by means of the correction formula

\[ A_{353}^{(corr.)} = \frac{A_{353} \times 3.6 - A_{420}}{3.5} \]

Ratios of Absorbancies

<table>
<thead>
<tr>
<th>Chloride</th>
<th>( A_{420}/A_{353} = 0.082 )</th>
<th>( A_{470}/A_{353} = 0.015 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromide</td>
<td>( A_{420}/A_{353} = 3.6 )</td>
<td>( A_{470}/A_{353} = 2.3 )</td>
</tr>
<tr>
<td>Iodide</td>
<td>( A_{420}/A_{353} = 4.5 )</td>
<td>( A_{470}/A_{353} = 15 )</td>
</tr>
</tbody>
</table>
Table III
Summary of Statistical Runs
Twenty-five runs on solutions containing 12.5 mg./l. of Cl⁻

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample size ml.</th>
<th>Mg./l. of Cl⁻ found</th>
<th>Mean deviation from average</th>
</tr>
</thead>
<tbody>
<tr>
<td>A Mohr</td>
<td>100</td>
<td>13.04</td>
<td>±1.1%</td>
</tr>
<tr>
<td>B Mercuric Nitrate</td>
<td>100</td>
<td>12.13</td>
<td>±1.4%</td>
</tr>
<tr>
<td>C Spectrophotometric</td>
<td>2</td>
<td>12.45</td>
<td>±1.2%</td>
</tr>
</tbody>
</table>

Table IV
Effect of Treatment with Aluminum Hydroxide Suspension on Absorbancy of Water Sample

Absorbancy at 353 μm with respect to distilled water

<table>
<thead>
<tr>
<th>Untreated Sample</th>
<th>Treated Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.091</td>
<td>0.013</td>
</tr>
<tr>
<td>0.026</td>
<td>0.012</td>
</tr>
<tr>
<td>0.044</td>
<td>0.020</td>
</tr>
<tr>
<td>0.119</td>
<td>0.031</td>
</tr>
<tr>
<td>0.098</td>
<td>0.028</td>
</tr>
<tr>
<td>0.103</td>
<td>0.029</td>
</tr>
<tr>
<td>0.075</td>
<td>0.026</td>
</tr>
<tr>
<td>0.086</td>
<td>0.030</td>
</tr>
<tr>
<td>0.120</td>
<td>0.031</td>
</tr>
<tr>
<td>0.166</td>
<td>0.029</td>
</tr>
</tbody>
</table>
Table V

Determination of Chloride Ion in Natural Waters

<table>
<thead>
<tr>
<th>Sample No., Method</th>
<th>Sample size</th>
<th>Chloride found mg./l.</th>
<th>Mean deviation from average</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>4.95 (10)</td>
<td>3.8</td>
<td>5.5</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>3.9 (10)</td>
<td>3.7</td>
<td>4.4</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>4.15 (10)</td>
<td>3.9</td>
<td>4.5</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>4.8 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>3.5 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C**</td>
<td>2</td>
<td>4.7 (8)</td>
<td>4.4</td>
<td>4.9</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>11.6 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>10.2 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C**</td>
<td>2</td>
<td>11.4 (8)</td>
<td>11.3</td>
<td>11.5</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>19.8 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>18.2 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C**</td>
<td>2</td>
<td>19.0 (8)</td>
<td>18.6</td>
<td>19.4</td>
</tr>
<tr>
<td>A</td>
<td>100</td>
<td>22.9 (8)</td>
<td>22.5</td>
<td>23.2</td>
</tr>
<tr>
<td>B</td>
<td>100</td>
<td>21.8 (10)</td>
<td>21.3</td>
<td>22.1</td>
</tr>
<tr>
<td>C**</td>
<td>2</td>
<td>22.2 (10)</td>
<td>21.8</td>
<td>22.8</td>
</tr>
<tr>
<td>A</td>
<td>50</td>
<td>128.8 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>50</td>
<td>128.0 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C**</td>
<td>1</td>
<td>125 (8)</td>
<td>124</td>
<td>127</td>
</tr>
<tr>
<td>A</td>
<td>10</td>
<td>610 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>10</td>
<td>636 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>591 (8)</td>
<td>585</td>
<td>596</td>
</tr>
<tr>
<td>A</td>
<td>5</td>
<td>1201 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>6</td>
<td>1200 (3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1</td>
<td>1180 (8)</td>
<td>1170</td>
<td>1189</td>
</tr>
</tbody>
</table>

A-Mohr, B-Mercuric Nitrate, C-Spectrophotometric
( ) indicates number of runs
** Sample was treated with aluminum hydroxide
### Table VI

**Determination of Chloride in Natural Waters**

**Blended with Synthetic Sodium Chloride Solution**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Chloride ion concentration (theoretical) mg/l.</th>
<th>Method</th>
<th>Chloride ion concentration determined (average)</th>
<th>Mean deviation from average</th>
<th>Error with respect to theoretical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 a</td>
<td>24.05</td>
<td>A</td>
<td>24.5 (2)</td>
<td>±1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>22.9 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>23.8 (8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 b</td>
<td>44.0</td>
<td>A</td>
<td>43.6 (2)</td>
<td>±0.3</td>
<td>-1.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>44.0 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>43.2 (8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 c</td>
<td>103.7</td>
<td>A</td>
<td>104.3 (3)</td>
<td>±0.6</td>
<td>-1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>103</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>102.5 (8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 a</td>
<td>32.0</td>
<td>A</td>
<td>32.4 (2)</td>
<td>±0.1</td>
<td>-0.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>31.6 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C**</td>
<td>31.8 (8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 b</td>
<td>41.8</td>
<td>A</td>
<td>41.5 (2)</td>
<td>±0.7</td>
<td>-0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
<td>42.5 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C**</td>
<td>41.5 (8)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A-Mohr, B-Mercuric Nitrate, C-Spectrophotometric

( ) indicates number of runs  ** Sample was treated with aluminum hydroxide
Table VII

Effect of Relative Humidity of Air at 25° C upon Volume of Reagent in Bubbler, and Resulting Error

<table>
<thead>
<tr>
<th>% relative humidity of air</th>
<th>Concentration of HClO₄ in equilibrium with atmosphere M</th>
<th>Max. volume change (%) due to AV</th>
<th>Change in acidity due to ΔM</th>
<th>Max. error due to ΔM*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-4.0</td>
<td>+0.21</td>
<td>8.2</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-3.3</td>
<td>+0.17</td>
<td>6.7</td>
</tr>
<tr>
<td>20</td>
<td>8.1</td>
<td>-2.6</td>
<td>+0.14</td>
<td>5.4</td>
</tr>
<tr>
<td>30</td>
<td>7.3 *</td>
<td>-2.0</td>
<td>+0.10</td>
<td>4.0</td>
</tr>
<tr>
<td>40</td>
<td>6.5</td>
<td>-1.4</td>
<td>+0.07</td>
<td>2.8</td>
</tr>
<tr>
<td>50</td>
<td>5.8</td>
<td>-0.7</td>
<td>+0.03</td>
<td>1.3</td>
</tr>
<tr>
<td>60</td>
<td>5.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>70</td>
<td>4.3</td>
<td>+0.6</td>
<td>-0.03</td>
<td>-1.2</td>
</tr>
<tr>
<td>80</td>
<td>3.3</td>
<td>+1.2</td>
<td>-0.06</td>
<td>-2.4</td>
</tr>
<tr>
<td>90</td>
<td>2.1</td>
<td>+1.9</td>
<td>-0.10</td>
<td>-3.9</td>
</tr>
<tr>
<td>100</td>
<td>0.0</td>
<td>+2.5</td>
<td>-0.13</td>
<td>-5.1</td>
</tr>
</tbody>
</table>

* Calculated from change in volume

** Effect on background absorption neglected
Table VIII

Stability Constants of FeCl^{++}

<table>
<thead>
<tr>
<th>HClO₄</th>
<th>NaClO₄</th>
<th>Mg(ClO₄)₂</th>
<th>Ionic strength</th>
<th>p(H₂O) mm. Hg 25°C</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.50 M</td>
<td></td>
<td></td>
<td>2.51</td>
<td>20.81</td>
<td>4.2 ± 0.1</td>
</tr>
<tr>
<td>3.00 M</td>
<td></td>
<td></td>
<td>3.02</td>
<td>19.89</td>
<td>5.8 ± 0.1</td>
</tr>
<tr>
<td>4.00 M</td>
<td></td>
<td></td>
<td>4.06</td>
<td>17.47</td>
<td>12.5 ± 0.2</td>
</tr>
<tr>
<td>4.95 M</td>
<td></td>
<td></td>
<td>5.09</td>
<td>14.65</td>
<td>28.0 ± 0.3</td>
</tr>
<tr>
<td>6.00 M</td>
<td></td>
<td></td>
<td>6.29</td>
<td>11.21</td>
<td>92 ± 1.2</td>
</tr>
<tr>
<td>7.00 M</td>
<td></td>
<td></td>
<td>7.48</td>
<td>7.87</td>
<td>329 ± 4.0</td>
</tr>
<tr>
<td>8.00 M</td>
<td></td>
<td></td>
<td>8.75</td>
<td>4.91</td>
<td>1340 ± 25</td>
</tr>
<tr>
<td>8.50 M</td>
<td></td>
<td></td>
<td>9.45</td>
<td>-</td>
<td>2960 ± 50</td>
</tr>
<tr>
<td>9.00 M</td>
<td></td>
<td></td>
<td>10.17</td>
<td>-</td>
<td>6100 ± 100</td>
</tr>
<tr>
<td>4.95 M</td>
<td>0.775</td>
<td></td>
<td>5.94</td>
<td>12.90</td>
<td>52 ± 0.5</td>
</tr>
<tr>
<td>4.95 M</td>
<td>1.55</td>
<td></td>
<td>6.72</td>
<td>11.25</td>
<td>97 ± 1.4</td>
</tr>
<tr>
<td>4.95 M</td>
<td>2.32</td>
<td></td>
<td>7.58</td>
<td>9.62</td>
<td>184 ± 3.0</td>
</tr>
<tr>
<td>4.95 M</td>
<td>0.555</td>
<td></td>
<td>6.58</td>
<td>11.02</td>
<td>86 ± 1.2</td>
</tr>
<tr>
<td>4.95 M</td>
<td>1.03</td>
<td></td>
<td>8.06</td>
<td>7.96</td>
<td>240 ± 5</td>
</tr>
</tbody>
</table>
Figure 1
Variation of Absorbancy
with Perchloric Acid Concentration

Chloride concentration: 80 μg./10 ml.
Iron(III) concentration: 0.1 M - IA, IB
              0.02 M - IIA, IIB
Wave length: 350 мп

--- Reagents with respect to water
Influence of Iron(III) Concentration on Absorbancy

1. 17.5 mg./l. of chloride in 6 M $\text{HClO}_4$ (342 mµ)
2. 8.0 mg./l. of chloride in 8 M $\text{HClO}_4$ (350 mµ)
3. Blank corresp. to 1
4. Blank corresp. to 2
Figure 3
Absorption Spectra arising from the Presence of Bromide and Iodide Ion

1. 130 mg./l. I\(^-\)
2. 16 mg./l. Br\(^-\)
3. 130 mg./l. I\(^-\)
4. 1300 mg./l. I\(^-\) added, aqueous phase after extraction of excess ibdine into CCl\(_4\)
5. 80 mg./l. Br\(^-\)

Sol. 1 and 2:
0.01 M iron(III) in 8.5 M HClO\(_4\)

Sol. 3, 4, and 5:
0.1 M iron(III) in 2.5 M HClO\(_4\)
Figure 4
Absorption Spectra of Iron(III) Chloro Complex
and of Corresponding Blanks

1. 12 mg./l. Cl\(^-\), 0.01 M Fe(III) in 8.5 M HClO\(_4\)
2. 24 mg./l. Cl\(^-\), 0.1 M Fe(III) in 2.5 M HClO\(_4\)
3. Blank corresp. to 1
4. Blank corresp. to 2
Figure 5

Plot of Percentage Error against P.P.M. of Chloride in the Unknown

A - Mohr method
B - Mercuric Nitrate method
C - Spectrophotometric method

The broken line extending from curve C indicates the increase of % error if the unknown is not diluted.

Percentage Error

Chloride Concentration in the Unknown (mg./l.)
Figure 6

Gas Dilution Experiments

Plot of chloride concentration measured spectrophotometrically vs. chloride concentration calculated from volume of hydrogen chloride gas delivered from gas buret.

The broken line indicates the ideal values.
Figure 7
Continuous Variation Plot

Absorbancy vs. \( \frac{[\text{Cl}^{-}]}{[\text{Fe}^{3+}]} \)
Figure 8

Log K vs. Perchloric Acid Concentration

![Graph showing Log K vs. Perchloric Acid Concentration]
Figure 9

Log $K$ vs. Perchlorate Concentration

- $\square$ $\text{HClO}_4$
- $\bullet$ $\text{HClO}_4$ and $\text{NaClO}_4$
- $\bigcirc$ $\text{HClO}_4$ and $\text{Mg(}\text{ClO}_4\text{)}_2$
Figure 10

Log K vs. the Square Root of Ionic Strength

- □ HClO₄
- • HClO₄ and NaClO₄
- ○ HClO₄ and Mg(ClO₄)₂
Figure 11
Log K vs. Vapor Pressure of Water

- $\text{HClO}_4$
- $\text{HClO}_4$ and $\text{NaClO}_4$
- $\text{HClO}_4$ and $\text{Mg(ClO}_4)_2$
Figure 12

Log $K$ vs. Reciprocal Absolute Temperature

I - Medium: 3.0 M perchloric acid
II - Medium: 8.5 M perchloric acid
Figure 13

Absorption Spectra of FeCl^{2+} and Fe(III)
in 9 M Perchloric Acid

1 - 2\times10^{-4} \text{ M Cl}^{-}, 3.1\times10^{-4} \text{ M Fe(III)}
   with respect to 2\times10^{-4} \text{ M Fe(III)}

2 - 10^{-4} \text{ M Fe(III)} with respect to perchloric acid
Figure 14

Absorption Band of $5 \times 10^{-4}$ M Fe(III) in Perchloric Acid

1 - in 2.5 M acid
2 - in 5.0 M acid
3 - in 8.5 M acid

The spectra were recorded with respect to perchloric acid.
Figure 15
Change of FeCl$^{++}$ Concentration at Various Acidities
with Time of Exposure to Light

Relative Concentration of FeCl$^{++}$, Per Cent.

Time of Exposure (sec.)

3.0 M HClO$_4$
5.0 M
6.0 M
7.0 M
8.0 M
9.0 M
VITA

Hans Coll was born June 8, 1929, in Graz, Austria. He received his elementary education in Austria and graduated from Bundesrealgymnasium Bruck a. d. Mur in July, 1948.

In October, 1948, he enrolled as a student of chemistry at the University of Graz, Austria. He came to the United States in September, 1951, as an exchange student and was admitted to the Graduate School of Louisiana State University. After a study of one year at this school he spent the year 1952-1953 in Austria; he re-enrolled at Louisiana State University in September, 1953. He received the M.S. degree in chemistry in June, 1955.

At the present time he is a candidate for the degree of Doctor of Philosophy.
EXAMINATION AND THESIS REPORT

Candidate:  Hans Coll

Major Field:  Chemistry

Title of Thesis:  Spectrophotometric Determination of Chloride Ion

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

May 4, 1957