4. Data on the adsorption of oxygen by iron have been given.

5. Oxides of iron were found to be soluble in chromic acid solutions and oxide-covered wires could be made active by a reduction of pressure.

6. An adsorbed film of oxygen as a primary cause of passivity has been discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CITY COLLEGE OF NEW YORK]

Organic Reagents[1] in Qualitative Analysis. III. The Analysis of the Common Metals of the Alkaline Earth Group and Magnesium Using 8-Hydroxyquinoline

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In the field of qualitative analysis the detection of the alkaline earth metals, especially in small amounts, is one of the most difficult of all. Though a number of organic reagents have been suggested for this purpose, most of them have certain disadvantages which prevent their use in a scheme of analysis. Either they are not specific, or the presence of some other normally occurring metal interferes or else the reagent cannot be employed for separations. However, one organic substance, 8-hydroxyquinoline (oxin, 8-quinolinol), which has already been used as a precipitant for metals,[2] was found to be excellent reagent in the analysis of the group.

In this work a method of analysis of the alkaline earth metals and magnesium, using 8-hydroxyquinoline, has been developed which makes it possible to detect small amounts. In brief Ca^{++} and Mg^{++} are precipitated by the organic reagent in an ammoniacal solution containing ammonium salts. The Ca^{++} is then separated from Mg^{++} in acetic acid as the oxalate and the Mg^{++} reprecipitated as the 8-hydroxyquinoline salt by making the solution alkaline with ammonia. A distinct advantage of the use of 8-hydroxyquinoline is that any excess in the filtrate can be removed easily by evaporation, as it is apparently volatile with steam. The solution is then analyzed for Ba^{++} and Sr^{++} by one of the usual methods.

Together with the scheme of analysis a test has been worked out using tannic acid in an alkaline solution,[3] which gives a preliminary indication of the alkaline earth metals.

Experimental

1. **Reaction of Alkaline Earth and Alkali Metals with Tannic Acid in Alkaline Solution.**—To varying amounts from 1–500 mg. of the metals, separately, 1 ml. of 2% tannic acid solution was added and then made alkaline with 6 *M* sodium hydroxide solution. Ba^{++}, Sr^{++} and Ca^{++} gave blue-green solutions or precipitates while the others were tan colored; 1 mg. of Ba^{++}, Sr^{++} or Ca^{++} in the presence of 500 mg. of the others, except NH_4^+ gave the same result. When ammonium salts are present the solution is made distinctly alkaline with sodium hydroxide, carefully warmed until all the ammonia is volatilized and then the test is carried out. Thus 1 mg. of Ba^{++}, Sr^{++} and Ca^{++} in the presence of 500 mg. NH_4^+ gave a positive result.

2. **Reaction of Ba^{++}, Sr^{++}, Ca^{++} and Mg^{++} with 8-Hydroxyquinoline.**—Varying amounts from 1–500 mg. of each of the above, separately, were mixed with 5–30 ml. of saturated ammonium chloride solution, made alkaline with ammonia and 15% solution of 8-hydroxyquinoline in 6 *M* acetic acid[4] added, keeping the solution alkaline with concentrated ammonia, until no further precipitation took place. This is indicated by a yellow supernatant liquid. In order to distinguish a precipitate of a metal 8-hydroxyquinoline compound from that of the reagent itself, at first the solution was kept above the melting point, 73–74°, of the 8-hydroxyquinoline. However, it was found that the calcium salt is appreciably soluble in the hot solution. So, instead, a preliminary test was made using a saturated solution of the reagent in concentrated ammonia. The results of these experiments showed that Ca^{++} and Mg^{++} are completely precipitated while Ba^{++} and Sr^{++} are not precipitated at all.

Using the same procedure and various combinations of the metals, it was found that 1 mg. or more of Ca^{++} and Mg^{++} could be separated completely from 500 mg. of Ba^{++} or Sr^{++} or any combination of both. Similar results were obtained using Na^+ and K^+ instead of Ba^{++} and Sr^{++}.

However, when large amounts of Ca^{++} and Mg^{++} were precipitated in the presence of large amounts of Ba^{++} and Sr^{++}, as much as 5 mg. of Ba^{++} and Sr^{++} was adsorbed by the precipitate. Furthermore, in the presence of 500

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(1) Most of the organic reagents are made by the Eastman Kodak Co., Rochester, N. Y.

(2) "Organic Reagents for Metals," Hopkin & Williams, Ltd., London, Eng., p. 51.

(3) L. Rosenthaler, *Mikrochemie*, **14**, 363–368 (1934); G. Ammer and H. Schmitz, *Wasser*, **8**, II, 161–168 (1934).

(4) This solution was chosen in preference to alcohol and diluted acetic acid solutions as a result of experiments showing less volume of the precipitant would be necessary.

mg. of Ca^{++} or Mg^{++} or combination of both, only 2 mg. of Ba^{++} or 3 mg. of Sr^{++} in the original solution could be detected after the precipitation.[5]

3. **Separation of Ca^{++} and Mg^{++}.**—Various combinations of Ca^{++} and Mg^{++} from 1–500 mg. in a saturated ammonium chloride solution were precipitated with 8-hydroxyquinoline, keeping the solution alkaline with ammonia, filtered with suction and then dissolved with hot 3 *M* acetic acid. While still hot 0.25 *M* ammonium oxalate solution was added slowly with stirring until no further precipitation of the Ca^{++} took place. The mixture was filtered, the filtrate concentrated to 10 ml. by evaporation and divided in half. One half was tested for Mg^{++} with *p*-nitrobenzene–azoresorcinol and sodium hydroxide[6] and the other half by making alkaline with ammonia and adding a small volume of 8-hydroxyquinoline solution. The experiments showed that 1 mg. of either metal could be detected in the presence of 500 mg. of the other.

4. **Separation of Ba^{++} and Sr^{++}.**—Though this method is a standard one, experiments were carried out to determine how much of each could be detected. Different mixtures containing 1–500 mg. of each were precipitated with 2 *M* ammonium carbonate, filtered and dissolved in 1 *M* acetic acid. The solution was warmed and 0.5 *M* potassium chromate solution added slowly with stirring until no further precipitation occurred. After filtering, washing and concentrating the filtrate, it was tested for Sr^{++} with ammonium oxalate solution. The results showed that 1 mg. of either metal could be detected in the presence of 500 mg. of the other.

On the basis of the above experiments a method of analysis was worked out and various combinations of the four metals from 1–500 mg. analyzed. The results confirmed those found above, *viz.*, that 1 mg. of Ca^{++} and Mg^{++} could be detected in the presence of 500 mg. of any other or combination of others; that 2 mg. of Ba^{++} and 3 mg. of Sr^{++} are detectable in the presence of 500 mg. of Ca^{++} or Mg^{++} or combination of both.

5. **Method of Analysis.**—The filtrate from the ammonium sulfide group, after acidification with acetic acid and removal of hydrogen sulfide, is evaporated to 25 ml. and filtered, if necessary. A small portion, 5 ml., is made alkaline with concentrated ammonia and a saturated solution of 8-hydroxyquinoline in ammonia added to test for the presence of Ca^{++} and Mg^{++}. If present, the test portion is combined with the main solution, made alkaline with concentrated ammonia and 15% solution of 8-hydroxyquinoline in 6 *M* acetic acid slowly added, keeping the solution alkaline with concentrated ammonia, until no further precipitation occurs. This is indicated by a yellow supernatant liquid. The mixture is filtered using suction and the precipitate washed twice with dilute ammonia, the washings being combined with the filtrate (filtrate B).

Residue.—The precipitate is dissolved in the smallest volume of hot 3 *M* acetic acid. While still hot, 1 *M* ammonium sulfate solution is added slowly with stirring to precipitate any Ba^{++} and Sr^{++} that had been adsorbed,[7] the solution filtered, the residue washed and then discarded. The filtrate is heated and 0.5 *M* ammonium oxalate solution slowly added with stirring until no further precipitation, showing the presence of Ca^{++}, takes place, filtered and washed (filtrate A).

Filtrate A.—A small portion is first tested for magnesium with *p*-nitrobenzene-azoresorcinol and sodium hydroxide. If positive, the remainder of the solution is made alkaline with ammonia and a small volume of the 8-hydroxyquinoline solution added, keeping the solution alkaline with ammonia. A yellow precipitate indicates Mg^{++}.

Filtrate B.—The solution is evaporated to dryness and the ammonium salts volatilized by continual heating. After cooling, the residue is treated with a small amount of dilute hydrochloric acid and then a small volume of water is added. The solution is filtered, if necessary, and the filter paper washed. The solution is made alkaline with concentrated ammonia and ammonium carbonate added until no further precipitation occurs, filtered and washed (filtrate contains alkali group).

Residue.—Dissolve with 1 *M* acetic acid and test a small portion for Ba^{++} with 0.5 *M* potassium chromate solution.[8] If present, warm the solution and add the potassium chromate solution slowly until no further precipitation takes place. Filter and wash. The filtrate is evaporated to 10 ml. and 0.5 *M* ammonium oxalate solution added, a white precipitate indicating Sr^{++}.

Summary

A preliminary test, using tannic acid, has been worked out, which can indicate 1 mg. of the alkaline earth metals even in the presence of large amounts of ammonium salts.

A method of analysis of the alkaline earth metals and magnesium, using 8-hydroxyquinoline, has been developed so that 1 mg. of Ca^{++} and Mg^{++}, 2 mg. of Ba^{++} and 3 mg. of Sr^{++} can be detected in the presence of 500 mg. of any other metal of this group or combination of others.

In the method of analysis Ca^{++} and Mg^{++} are separated from Ba^{++} and Sr^{++} by precipitating with 8-hydroxyquinoline in an ammoniacal solution. The Ca^{++} is separated from Mg^{++} as oxalate in acetic acid and the magnesium reprecipitated as the 8-hydroxyquinoline salt by making alkaline with ammonia. Ba^{++} and Sr^{++} are analyzed by one of the usual accepted methods.

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(5) If the Ca^{++} and Mg^{++} 8-hydroxyquinoline precipitates are dissolved in acetic acid and reprecipitated with ammonia all the adsorbed Ba^{++} and Sr^{++} can be removed.

(6) (a) K. Suitzu and K. Okuma, *J. Soc. Chem. Ind., Japan*, **29**, 132 (1926); (b) Feigl, "Qualitative Analyse mit Hilfe von Tüpfel-Reaktionen," Akademische Verlagsgesellschaft, Leipzig, Germany, 1935, 2d ed., p. 262.

(7) As the largest amount of Ba^{++} and Sr^{++} adsorbed does not exceed 5 mg., only a small volume of ammonium sulfate solution is necessary and practically no Ca^{++} is precipitated. If very small amounts of Ba^{++} and Sr^{++} are to be detected, the 8-hydroxyquinoline precipitate should be dissolved in acetic acid and reprecipitated with ammonia.

(8) If Ba^{++} is absent, a sensitive test for Sr^{++} can be immediately performed by treating with a saturated water solution of tetrahydroxyquinone, a reddish-brown precipitate indicating its presence [G. Gutzeit, *Helv. Chim. Acta*, **12**, 728 (1929)].