manganese than that employed above. The results obtained are given below:

TABLE VII.

Parts Mn.	Parts Fe.	Color.	Result.
1 (0.2 mg.)	500	Reddish pink	Good
1 (0.2 mg.)	1000	Reddish yellow	Fair
1 (0.2 mg.)	2000	Reddish brown	Doubtful[1]

From the results of Tables VI and VII it appears that the lead dioxide test for manganese is unreliable in the presence of three or four hundred parts of iron, unless a fairly large amount of manganese is present such as 0.2 mg. when a somewhat larger ratio of iron does not interfere with the test. On the other hand, the bead test is efficient with larger amounts of iron provided enough manganese (0.005 mg.) is introduced into the bead and provided the precautions cited under Table IV are followed.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL CHEMISTRY, COLLEGE OF THE CITY OF NEW YORK.]

THE DETERMINATION OF THE SENSITIVENESS OF THE HYDROXIDE REACTIONS FOR THE COMMON METALS.[2]

BY L. J. CURTMAN AND A. D. ST. JOHN.

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The hydroxide reactions of the metals are perhaps the most common as well as the most important of those which take place in the wet way; yet no systematic work has been done to determin the delicacy of these reactions. The present work was therefore undertaken to supply this information, the need for which was felt in qualitative work. From the fact that the hydroxides studied were formed by precipitation, it might appear that the desired results could be calculated from the figures for the respective solubility products of the hydroxides; but it unfortunately happens that, with few exceptions, these figures have not as yet been determined; moreover, this information, even if available, would give but a rough idea of the sensitivity limit, for the reason that the final result of a sensitivity determination is largely an optical phenomenon that is controlled by factors, some of which are not included in the law of mass action. Chief among these factors are those which affect the visibility of the precipitate in very dilute solutions; such as its form, density, and color. In order to obtain comparable results, all the experiments were carried out under uniform conditions. The general procedure was as

[1] The color given by the last test could not be readily distinguished from a solution containing 400 mg. of Fe as $Fe(NO_3)_3$ in 5 cc. It may also be noted that a solution of this concentration of iron was noticeably decolorized by the nitric acid and lead dioxide treatment.

[2] Read before Section I (Analytical Chemistry) of the Eighth International Congress of Applied Chemistry, September 11, 1912.

follows: In separate experiments diminishing amounts of metal, in the form of a solution of one of its salts, were treated in test tubes with a slight excess of a 10% solution of either ammonia or sodium hydroxide, depending upon the solubility of the precipitate in an excess of either, and the tubes examined for a precipitate. The final volume in each case, including the reagent added, was 5 cc. The following results were obtained:

Lead.—A standard solution of lead nitrate containing a trace of nitric acid was employed in these tests. The precipitant was a 10% solution of ammonia. The results are tabulated below:

	Cold.	Boiled.
5 cc. = 25.0 mg. Pb	Large precipitate	Large precipitate
5 cc. = 12.5 mg. Pb	Slight precipitate	Large precipitate
5 cc. = 5.0 mg. Pb	Cloudiness	Small precipitate
5 cc. = 2.5 mg. Pb	Slight cloudiness	Slight precipitate
5 cc. = 1.0 mg. Pb	Very faint cloudiness	Slight cloudiness
5 cc. = 0.75 mg. Pb	Just visible cloudiness	Limit

The most uniform results were obtained by boiling. The precipitate was white and divided. The result obtained with 0.75 mg. of lead was just visible without eye strain and represents a concentration of one part in 6500. No hydrolysis was observed in blanks either in the cold or on boiling.

Silver.—A solution of silver nitrate was employed in these tests. The precipitant was a 10% solution of sodium hydroxide. All samples were boiled. The following results were obtained:

5 cc. = 25.0 mg. Ag	Heavy precipitate
5 cc. = 5.0 mg. Ag	Slight precipitate
5 cc. = 2.5 mg. Ag	Cloudiness
5 cc. = 1.0 mg. Ag	Slight cloudiness
5 cc. = 0.5 mg. Ag	Faint cloudiness
5 cc. = 0.25 mg. Ag	Faint cloudiness
5 cc. = 0.125 mg. Ag	Limit

The end product was brownish. The limit test was given by a solution of silver, the concentration of which was one part in 40,000.

Mercury (= ous).—A solution of mercurous nitrate, containing approximately 1% of concentrated nitric acid, was employed in these tests. The following results were obtained:

	NaOH.	NH_4OH.
5 cc. = 25.0 mg. Hg	Large precipitate	Large precipitate
5 cc. = 5.0 mg. Hg	Heavy precipitate	Heavy precipitate
5 cc. = 2.5 mg. Hg	Heavy precipitate	Heavy precipitate
5 cc. = 1.0 mg. Hg	Slight precipitate	Slight precipitate
5 cc. = 0.5 mg. Hg	Slight precipitate or coloration	Very faint precipitate which increases on standing

	NaOH.	NH_4OH.
5 cc. = 0.25 mg. Hg	Slight precipitate or coloration	Limit on standing two minutes
5 cc. = 0.10 mg. Hg	Very slight precipitate or coloration	
5 cc. = 0.05 mg. Hg	Very faint precipitate or coloration	
5 cc. = 0.025 mg. Hg	Limit. Appears light gray, away from the source of light	

The above results indicate that a 10% sodium hydroxide solution is a more sensitive reagent for the detection of mercurous mercury than an ammoniacal solution of the same strength. With the former the limiting test was given by a solution whose concentration was one part in 200,000 while with the latter reagent the limit was one part in 20,000.

Mercury (= ic).—The following results were obtained with a solution of mercuric chloride:

	NaOH.	NH_4OH.
5 cc. = 25.0 mg. Hg	Heavy precipitate	Heavy precipitate
5 cc. = 12.5 mg. Hg	Slight precipitate	Fair sized precipitate
5 cc. = 5.0 mg. Hg	Slight precipitate	Slight precipitate
5 cc. = 2.5 mg. Hg	Limit	Slight precipitate
5 cc. = 1.0 mg. Hg		Coloration $^1/_2$ minute
5 cc. = 0.5 mg. Hg		Slight coloration $^1/_2$ minute
5 cc. = 0.375 mg. Hg		Limit

The precipitates obtained with sodium hydroxide were yellow, becoming orange with dilution. With ammonia the precipitates were white.

The limiting results obtained above show that with sodium hydroxide one part of mercury in 2,000 can be detected while with ammonia the delicacy is one part in 13,000.

Bismuth.—In the following tests, a solution of bismuth nitrate acid with nitric acid was used. The following results were obtained with ammonia as the precipitant:

	Cold.	Boiled.
5 cc. = 25.0 mg. Bi	White gelatinous precipitate	White gelatinous precipitate
5 cc. = 5.0 mg. Bi	White gelatinous precipitate	White gelatinous precipitate[1]
5 cc. = 2.5 mg. Bi	Slight gelatinous precipitate	White gelatinous precipitate[1]
5 cc. = 1.0 mg. Bi	Limit	Faint precipitate
5 cc. = 0.5 mg. Bi		Limit

In the cold it was found difficult to estimate the quantity of gelatinous precipitates; boiling facilitates this. The sensitiveness of the test in a boiling solution is shown to be one part in 10,000.

Copper.—The following results were obtained with a solution of copper nitrate using a sodium hydroxide solution as the precipitant:

[1] The precipitate coagulated and settled.

	Cold.	Boiled.
5 cc. = 25.0 mg. Cu	Heavy precipitate	Heavy precipitate
5 cc. = 5.0 mg. Cu	Light precipitate	Light precipitate which settles
5 cc. = 2.5 mg. Cu	Slight precipitate	Slight precipitate which settles
5 cc. = 1.0 mg. Cu	Limit	Faint precipitate
5 cc. = 0.5 mg. Cu		Limit

In the cold the color of the precipitates was bluish white; when boiled they were black becoming brown on dilution. The limit test in a boiling solution shows a delicacy of one part in 10,000.

Cadmium.—A solution of cadmium nitrate was employed in these tests with sodium hydroxide solution as the precipitant. The results obtained are given below:

	Cold.	Boiled.
5 cc. = 25.0 mg. Cd	Heavy precipitate	Heavy precipitate (white)
5 cc. = 5.0 mg. Cd	Heavy precipitate	Heavy precipitate which settled
5 cc. = 2.5 mg. Cd	Slight precipitate	Slight precipitate which settled
5 cc. = 1.0 mg. Cd	Cloudiness	Cloudiness
5 cc. = 0.5 mg. Cd	Slight cloudiness	Cloudiness
5 cc. = 0.25 mg. Cd	Faint cloudiness	Slight cloudiness
5 cc. = 0.125 mg. Cd	Limit	Limit

In all the above experiments in which less than one milligram was present in 5 cc., more conspicuous results were obtained on standing one minute. The limit tests show this reaction to possess a delicacy of one part in 40,000.

Iron.—The following results were obtained with a solution of ferric chloride. The precipitant chosen was ammonia.

5 cc. = 25.0 mg. Fe	Heavy precipitate
5 cc. = 5.0 mg. Fe	Heavy precipitate
5 cc. = 2.5 mg. Fe	Light precipitate
5 cc. = 1.0 mg. Fe	Light precipitate which looks like a coloration
5 cc. = 0.5 mg. Fe	Light precipitate which looks like a coloration
5 cc. = 0.25 mg. Fe	Very light precipitate which looks like a coloration
5 cc. = 0.125 mg. Fe	Faint color
5 cc. = 0.062 mg. Fe	Limit

On boiling, the precipitate becomes darker brown, and is more noticeable in small amounts. All the precipitates in quantities greater than one milligram coagulate and settle on boiling. The limiting test above shows the test to be exceedingly sensitive, producing a visible result in a concentration of one part in 80,000.

Aluminium.—All the results given below were obtained with a solution of aluminium chloride to which a slight excess of ammonia was added and the mixture boiled in each case:

5 cc. = 25.0 mg. Al	Heavy gelatinous precipitate
5 cc. = 5.0 mg. Al	Heavy gelatinous precipitate
5 cc. = 2.5 mg. Al	Light precipitate
5 cc. = 1.0 mg. Al	Light precipitate

5 cc. = 0.5 mg. Al	Very light precipitate
5 cc. = 0.25 mg. Al	Very light precipitate
5 cc. = 0.125 mg. Al	Faint precipitate
5 cc. = 0.05 mg. Al	Limit

With amounts greater than 0.5 mg. the precipitates coagulated in one or more isolated clots. With smaller amounts, however, the precipitates do not coagulate in large pieces but remain in a finely divided state. The delicacy of the test is one part in 100,000.

Chromium.—A solution of chromium nitrate was employed in the tests given below:

	NaOH.	NH_4OH.
5 cc. = 25.0 mg. Cr	Heavy precipitate (green)	Heavy precipitate (gray)
5 cc. = 5.0 mg. Cr	Medium sized precipitate	Medium sized precipitate
5 cc. = 2.5 mg. Cr	Slight precipitate	Slight precipitate
5 cc. = 1.0 mg. Cr	Faint precipitate	Slight precipitate
5 cc. = 0.5 mg. Cr	Limit	Very slight precipitate
5 cc. = 0.25 mg. Cr		Very slight precipitate
5 cc. = 0.125 mg. Cr		Very slight precipitate
5 cc. = 0.06 mg. Cr		Faint precipitate
5 cc. = 0.03 mg. Cr		Limit

All the precipitates were boiled and allowed to settle. With the lower amounts of metal the precipitates were slightly coagulated; while in the limiting tests the precipitates showed a decided tendency to form in the finely divided state. The limit test shows a delicacy of one in 170,000.

Zinc.—The following results were obtained with a solution of zinc nitrate. Ammonia was used in slight excess and the mixture boiled:

5 cc. = 25.0 mg. Zn	Dense white precipitate
5 cc. = 5.0 mg. Zn	Dense white precipitate
5 cc. = 2.5 mg. Zn	Slight precipitate
5 cc. = 1.0 mg. Zn	Slight precipitate
5 cc. = 0.5 mg. Zn	Slight precipitate
5 cc. = 0.25 mg. Zn	Cloudiness
5 cc. = 0.12 mg. Zn	Faint cloudiness
5 cc. = 0.06 mg. Zn	Limit

The limit test shows a delicacy of one part in 80,000.

Nickel.—A solution of nickel chloride was employed in carrying out the following tests. The precipitant was sodium hydroxide:

5 cc. = 25.0 mg. Ni	Heavy gelatinous precipitate (light green)
5 cc. = 5.0 mg. Ni	Slight precipitate
5 cc. = 2.5 mg. Ni	Slight precipitate
5 cc. = 1.0 mg. Ni	Slight precipitate
5 cc. = 0.5 mg. Ni	Few flakes
5 cc. = 0.25 mg. Ni	Few flakes
5 cc. = 0.125 mg. Ni	Few flakes
5 cc. = 0.06 mg. Ni	Limit

Not less than 0.5 mg. can be readily distinguished without boiling. The limit test shows a delicacy of one part in 80,000.

Cobalt.—For these tests a solution of cobalt nitrate was used. The reagent was sodium hydroxide.

5 cc. = 25.0 mg. Co	Heavy precipitate (blue becoming a dirty orange), coagulates and settles on boiling
5 cc. = 5.0 mg. Co	Heavy precipitate
5 cc. = 2.5 mg. Co	Slight precipitate
5 cc. = 1.0 mg. Co	Slight precipitate
5 cc. = 0.5 mg. Co	Very slight precipitate
5 cc. = 0.25 mg. Co	Faint precipitate
5 cc. = 0.125 mg. Co	Faint precipitate
5 cc. = 0.06 mg. Co	Limit.

Not less than 0.25 mg. can be seen in the cold. The limit test shows a concentration of one part in 80,000.

Manganese.—The following results were obtained with a solution of manganese chloride. In each test a slight excess of ammonia was added and the mixture boiled.

5 cc. = 25.0 mg. Mn	Heavy precipitate (orange)
5 cc. = 5.0 mg. Mn	Heavy precipitate (red-brown)
5 cc. = 2.5 mg. Mn	Medium sized precipitate
5 cc. = 1.0 mg. Mn	Slight precipitate (dark red)
5 cc. = 0.5 mg. Mn	Slight precipitate (black)
5 cc. = 0.25 mg. Mn	Slight precipitate (black)
5 cc. = 0.12 mg. Mn	Faint precipitate (black)
5 cc. = 0.06 mg. Mn	Faint precipitate (black)
5 cc. = 0.03 mg. Mn	Limit

With sodium hydroxide as reagent, the same results were obtained. With 5.0 mg. and less, the precipitate appears like a coloration before boiling.

The limit test shows a delicacy of one part in 170,000.

Magnesium.—A solution of magnesium sulfate was used in these tests with sodium hydroxide as the precipitant.

5 cc. = 25.0 mg. Mg	Heavy gelatinous precipitate
5 cc. = 5.0 mg. Mg	Heavy gelatinous precipitate
5 cc. = 2.5 mg. Mg	Heavy gelatinous precipitate
5 cc. = 1.0 mg. Mg	Slight precipitate
5 cc. = 0.5 mg. Mg	Limit

The limit test shows a delicacy of one part in 10,000.

THE COBALTINITRITE METHOD OF DETERMINING POTASSIUM.

By F. H. MACDOUGALL.

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In the usual way of determining potassium by the cobaltinitrite method, the yellow precipitate, supposed to have the composition represented by the formula $K_2NaCo(NO_2)_6.xH_2O$, is boiled with excess of 0.1 *N* $KMnO_4$ for several minutes, dilute sulfuric acid is added, then oxalic