A STUDY OF CERTAIN METAL PEROXIDES AND THEIR APPLICATIONS IN IODOMETRIC ANALYSES

by

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INTRODUCTION

This thesis is divided into two main sections. The first deals with the methods of preparation of several of the heavier metal peroxides. The second section is concerned mainly with some applications of zirconium peroxide in iodometric analyses.

Previous work on the more uncommon metal peroxides has been rather limited. Some of these metal peroxides were reported as early as 1849 (Gmelin, 6). Early investigators reported peroxides of cerium, titanium, zirconium, hafnium, and thorium could exist and postulated a formula of MO_3 for the peroxides (Schwarz, 16). Later studies on thorium peroxide (7, 8, 11, 12) and titanium (1, 2, 3, 17) peroxide showed the formulas were not as simple as the earlier investigators postulated. It was reported that the composition of the peroxides varied according to the methods of preparation.

Since the peroxides were precipitated as hydrated compounds, usually of a slimy, gelatinous nature, the determination of their composition was difficult. Several different methods (Billy, 4) were suggested to overcome this difficulty. In one case (Biltz, 5), the application of ammonia extraction was used in studies as a means of removing all except the chemically bound water from the product. Later studies of uranium peroxide (13, 15) and thorium peroxide (Thorne, 18) showed further that the empirical formula, MO_3, fitted few, if any, of the true peroxide compositions. The fact that some of the peroxides were unstable over a period of time further complicated the work. In

this thesis, a method of preparation was used which gave a product that was much easier to study. Analysis of some of the zirconium and thorium peroxides made, verified some of the assumptions brought out by earlier investigators.

PREPARATION OF PEROXIDES

Homogeneous Precipitation

Zirconium Peroxide Preparation. The zirconium peroxide was prepared in a three liter, three-neck distilling flask in which a motor-driven glass stirring rod was placed in the center opening. The solutions necessary for the preparation were added through the opening that was closed by a glass stopper. A solution of zirconyl chloride, 30 percent hydrogen peroxide, and urea, was placed in the flask and heated to boiling while stirring. As the urea slowly decomposed and raised the pH of the solution, a chunky, gelatinous precipitate of the peroxide was formed.

It was found that the character of the precipitate depended upon the pH of the reaction solution. To find the optimum conditions for precipitation, the amount of urea used was varied while the compositions of the zirconyl chloride solution and the hydrogen peroxide solution were kept constant. Twenty-five grams of C.P. grade zirconyl chloride octahydrate were put into solution in one liter of water, and 40 milliliters of 30 percent hydrogen peroxide, and the solid urea were added. With 7.5 grams of urea, a pH of 2.0 was reached after boiling for four hours. This gave a white, turbid solution, but no precipitate settled in

the flask. When the amount of urea was increased to 15 grams, and the solution boiled for one hour and forty minutes, a pH of 4.2 was obtained and a fine, white, gelatinous precipitate settled and was filtered from the solution and washed with suction. When this hydrated precipitate was dried in an oven at 90° C. it gave hard translucent chunks. The oxidizing action of this product on cadmium iodide-linear starch reagent was slow and weak (Lambert, 19).

By continuing this process, it was found that a solution of 25 grams of zirconyl chloride hydrate, 25 grams of urea, and 40 milliliters of 30 percent hydrogen peroxide in one liter of water gave the most active product. With this solution, a turbidity appeared after forty minutes of boiling and precipitation was complete after boiling for one hour and twenty-five minutes. The solution had a pH of 7.0 and gave a chunky, white precipitate that could be easily washed and filtered. After drying in a 100° C. oven for 5 hours, a hard, white, translucent product was obtained. The yield was 11.5 grams. The zirconium peroxide chunks fractured when placed in water, but were insoluble. It had a vigorous oxidizing effect on the cadmium iodide-linear starch reagent and decomposed when heated to give the white or tan oxide depending on the decomposition temperature.

Thorium Peroxide Preparation. The method of homogenous precipitation was used also to make thorium peroxide. The same apparatus described in the zirconium peroxide preparation was used to prepare the thorium peroxide. Twenty-five grams of

thorium nitrate in one liter of water, and 40 milliliters of 30 percent hydrogen peroxide were mixed in the reaction flask. This formed a heavy, viscous, turbid solution. Forty grams of urea were then added and the solution boiled, with stirring, for one hour. The solution had a pH of 7.0 and a granular, hydrated, white precipitate settled to the bottom of the flask. The precipitate was filtered with suction and washed several times with water. It was then placed in an oven for eleven hours at 90° C.. The resulting hard, glassy, chunks had a light blue-green color, gave a vigorous oxidizing action with cadmium iodide-linear starch reagent, and decomposed when heated to give the white oxide. A yield of 12 grams of the dried peroxide was obtained.

Titanium Peroxide Preparation. The peroxide of titanium was prepared in a manner identical to that used to form the peroxides previously discussed. Three hundred milliliters of a saturated solution of titanium sulfate were placed in a three-neck distilling flask and 15 milliliters of 30 percent hydrogen peroxide were added to the solution. As the hydrogen peroxide was added, the solution became yellow-orange in color. Seven and one-half grams of urea were then added and the solution boiled and stirred for one hour. After that period of time, a yellow precipitate was filtered from the reaction solution, washed with hot water, and dried in an oven at 85° C.. The precipitate dried to a yellow granular form, readily oxidized cadmium iodide-linear starch reagent, and decomposed when heated to give the white oxide.

Tin Peroxide Preparation. In the tin peroxide preparation, 25 grams of stannic chloride hydrate, 40 grams of urea, and 40 milliliters of 30 percent hydrogen peroxide were placed in one liter of water, and the solution placed in a three-neck distilling flask. When heat was applied, the solution became turbid. After an hour of boiling, a pH of 7.0 was reached and the white gelatinous precipitate that formed was filtered, washed with hot water, and dried in an oven at 70° C.. The hard, glassy, precipitate obtained oxidized the cadmium iodide-linear starch reagent, fractured in water, and decomposed when heated to give the white oxide.

Cadmium Peroxide Preparation. Twenty grams of cadmium nitrate hydrate, 45 grams of urea, and 45 milliliters of 30 percent hydrogen peroxide, were placed in one liter of water, and the clear solution boiled in a three-neck distilling flask. A turbidity appeared when the solution was heated initially. The turbid solution was boiled until a pale yellow precipitate formed. The precipitate was filtered, washed with hot water, and dried in an oven at 75° C.. The yellow granular product obtained oxidized the cadmium iodide-linear starch reagent and decomposed when heated to give the brown oxide.

Uranium Peroxide Preparation. This peroxide was easily obtained without using urea to raise the pH of the solution. Six grams of uranyl acetate dihydrate were put in solution in 400 milliliters of water. When 20 milliliters of 30 percent hydrogen peroxide were added, a yellow precipitate formed. The

resulting mixture was boiled for one hour, filtered, and washed with hot water. The precipitate was dried in an oven at 75° C., and formed a yellow, granular powder. This powder oxidized the cadmium iodide-linear starch reagent and decomposed when heated to give the red oxide of uranium.

Basic Precipitation

Cerium and Lanthanum Peroxides Preparation. Cerium and lanthanum peroxides were precipitated from a hydrogen peroxide solution by adding ammonium hydroxide. In the cerium peroxide precipitation, 40 milliliters of 30 percent hydrogen peroxide were added to a solution of 14 grams of ceric ammonium nitrate in one liter of water. A red solution was formed. When 10 milliliters of ammonium hydroxide were added, a chunky red precipitate was obtained which was filtered, washed, and dried in an oven at 70° C.. The peroxide decomposed in three months to give a light yellow powder.

In the lanthanum peroxide preparation, 1.9 grams of lanthanum ammonium nitrate were placed in a solution of 250 milliliters of water and 5 milliliters of 30 percent hydrogen peroxide. The solution was made basic with ammonium hydroxide and the resulting precipitate was filtered and washed. When dried in an oven at 50° C. white translucent chunks were formed which oxidized the cadmium iodide-linear starch reagent. The peroxide decomposed when heated to give the white oxide.

PROPERTIES OF PEROXIDES

Decomposition

Decomposition temperatures of some of the peroxides were obtained by placing them in a melting point tube bent in a U shape. The tube was fastened to a thermometer and placed in an oil bath so that the open end of the tube was under the surface. As the oil bath was heated, the peroxide decomposed, and the temperature which caused a rapid gas evolution was noted.

Table 1. Decomposition Temperatures

Peroxide	Temperature	Color of Oxide
Thorium	120° C	White
Cadmium	200°	Brown
Titanium	140°	White
Zirconium	140°	White
Uranium	180°	Red
Tin	120°	White

X-ray Diffraction

X-ray diffraction work by Dr. R. D. Dragsdorf, of Kansas State College, showed the peroxides of cadmium and uranium had definite crystal structures which gave characteristic lines in the diffraction patterns. The peroxides of thorium, cerium, and tin, gave broad, faint lines and showed very small crystal formation. Zirconium peroxide was found to be amorphous in structure since a broad, faint band was obtained which indicated no crystal formation.

Infrared Determinations

Infrared spectra determinations of zirconium, thorium, and tin peroxides, by Mr. W. G. Fately, Kansas State College, gave some information concerning the structure of these compounds. Peroxides of zirconium, thorium, and tin were studied. A peroxidic oxygen bond was shown in the area of 900 wave numbers. Metal-oxygen bonds were shown for all of the peroxides at wave number values approximating 1020, 1040, and 1100. Free -OH bonds were shown at 3400 wave numbers; and only a small amount of bonded -OH was indicated. Comparison of the peroxide content showed thorium peroxide to contain the greatest amount, followed by zirconium and tin peroxides.

Stability

All of these peroxides were insoluble in water. With the exception of zirconium and titanium peroxides, they dissolved readily in hot 6 N hydrochloric acid.

The oxidizing power of the peroxides varied greatly. The zirconium and thorium peroxides were the most active. When thorium peroxide was shaken in a test tube with solutions of iodide and bromide containing 100 ppm. of these ions and some carbon tetrachloride, the characteristic violet and red-brown colors due to iodine and bromine were obtained. When this procedure was repeated using zirconium peroxide, only the iodide solution was oxidized. Both the zirconium and thorium peroxides showed no apparent loss in activity after one year. Keeping the

zirconium peroxide under water for several months did not affect its oxidizing power or the mechanical properties of the granules. The other peroxides proved to be unstable at room temperature and after three to five months had lost most or all of their oxidizing power.

Analysis

The thorium peroxide was analyzed for the percent thorium by igniting to the oxide (9, 10, 14). The peroxide was found to be 71.5 percent thorium. The water content was determined by heating the compound at 120° C. and collecting the water driven off, in a calcium sulfate drying tube. The water in the peroxide was calculated to be 10.4 percent. A magnesium-potassium carbonate fusion test showed that no amine type nitrogen was present in the peroxide. On the basis of these determinations and the previous infrared work, the formula, $Th_2O_7.4H_2O$, was assigned to the thorium peroxide.

The zirconium peroxide was ignited to the oxide and the zirconium determined to be 59 percent. As a further check, the zirconium peroxide was dissolved in sulfuric acid, and the zirconium precipitated with cupferron. This precipitate was ignited to the oxide and the percent of zirconium determined. A value of 59 percent, which checked with the ignition method, was obtained. Analysis for water, by the previous method, gave a value of 15.5 percent. A magnesium-potassium carbonate fusion test showed that no amine type nitrogen was present in the

compound. The peroxide was checked for chloride and it was determined that very little was present. From these determinations and the infrared studies, a formula of $Zr_2O_5.3H_2O$ was assigned to the zirconium peroxide.

APPLICATION

Oxidizing Column

In the previous work it was noted that zirconium and thorium peroxides were the most active over a long period of time, and were insoluble in water. Of the two peroxides, zirconium was the more stable and had an amorphous structure. For these reasons, it was selected for further study. As this peroxide easily oxidized an iodide solution, it was used as an agent for quantitative determination of the iodide ion.

In the first attempts, zirconium peroxide was graded and a five centimeter column of the 100 mesh size was made in a burete. Twenty milliliter portions of iodide solutions ranging in concentrations from 1 to 25 ppm. were passed through the column at a rate of one drop every two seconds. The effluent iodine solution was collected and the column washed with two 10 milliliter portions of water which were added to the iodine solution. When the iodide solutions were added at the top of the column, a light tan ring formed at the top, indicating the oxidation reaction was occurring in the upper portion of the column. With this method, it was possible to oxidize the iodide solutions ranging in concentrations from 5 to 25 ppm. so that the final

solutions would give a light blue color when the cadmium iodide-linear starch reagent was added. It was noted that the water wash was not sufficient to rid the column of all the iodine formed. A light yellow color was still present after the two washings with water.

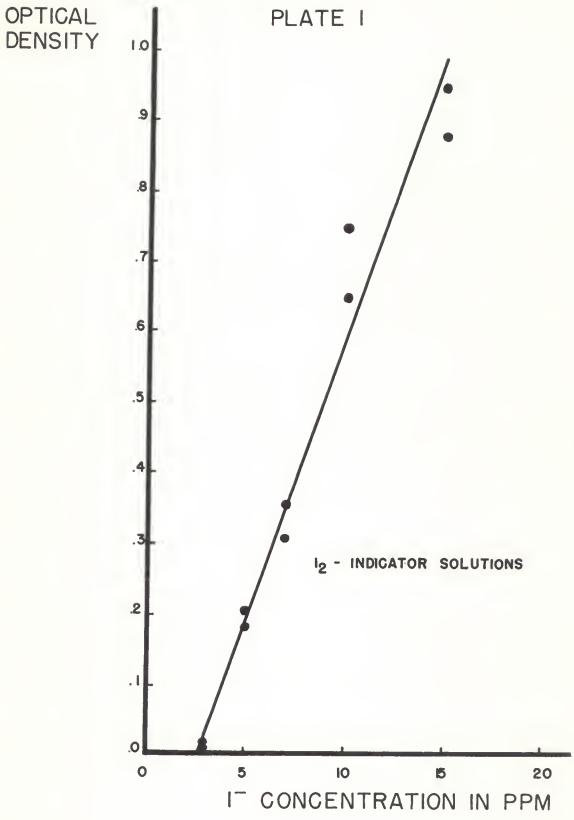
Another 5 centimeter column was made up using 100 mesh zirconium peroxide. Varying concentrations of iodide solutions were made with potassium bromide so that the final solutions were 5 percent potassium bromide by weight. The potassium bromide was added in an effort to help clean the iodine from the column by forming the I_2Br^- ion. A 50 milliliter portion of each solution was passed through the column at a rate of one drop every two seconds. The first 20 milliliters of solution coming through the column were discarded, and the next 20 milliliters were collected in a 50 milliliter volumetric flask. One milliliter of cadmium iodide-linear starch reagent was added and the solution made up to volume. The column was washed between runs with water until no iodine could be detected with the indicator. The optical densities of the collected solutions were read on a Beckman spectrophotometer at a wavelength of 615 millimicrons. It was found that the optical density values decreased with an increase in the iodide concentrations (Plate I). This indicated that in the more concentrated solutions an increasing percentage of the iodine was being held in the column.

The procedure was repeated using the same column. The curve obtained (Plate I) had the same form, but gave lower values for

EXPLANATION OF PLATE I

Optical densities of iodine solutions with starch indicator added.

PLATE I


OPTICAL DENSITY
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
5
10
15
20
I_2 - INDICATOR SOLUTIONS
I^- CONCENTRATION IN PPM

the same iodide concentrations. This indicated that the activity of the column was decreasing. This was proved by a third run which gave lower values than the two previous runs. From this data, it was assumed that the reaction was probably taking place on the surface of the zirconium peroxide granules in the column.

Several different attempts were made to reactivate the column. Washing the column with a .1 N hydrochloric acid solution increased the activity, but it was lost when more iodide solutions were passed through the column. Duplication of results could not be obtained by washing the column with .1 N hydrochloric acid and water prior to each run with a 20 ppm. iodide solution.

When 10 milliliters of a 3 percent hydrogen peroxide solution were passed through the column, it caused a vigorous bubbling reaction which generated heat. The gas given off from the zirconium peroxide column was oxygen. The column continued giving off oxygen after being washed several times with water.

Another column was made up using 200 mesh zirconium peroxide. This column behaved in a manner analagous to the 100 mesh column. After the activity had decreased, the column was treated with .1 N hydrochloric acid. Slow, thorough rinsing of the column with water resulted in a slight increase in the oxidizing power which was soon exhausted.

When 200 mesh thorium peroxide was used to make a column, it behaved similarly to the zirconium peroxide. The thorium peroxide column lost its activity faster than the zirconium

peroxide column. Its activity could also be increased by treatment with .1 N hydrochloric acid, but the effect was short lived. The lowest iodide concentration to give a blue color with the cadmium iodide-linear starch reagent after passing through the column, was a 2 ppm. solution.

A bromide solution was oxidized when passed through the thorium peroxide column, but the column lost its activity as before. A 4 ppm. bromide solution was oxidized by the column and gave a blue color with the cadmium iodide-linear starch reagent.

It was evident from the column work, that the oxidizing action took place on the surface of the particles of the peroxides. The peroxidic oxygen in the interior of the particles was not made available for reaction since the particles were hard and glassy. A large amount of the peroxides was necessary to form the column and the results did not warrant the expense.

Zirconium Peroxide Paper

The previous column work suggested that the oxidizing reactions took place on the surface of the peroxide particles. If this were true, a precipitated form of the zirconium peroxide, with a large surface area, would be more efficient. It was decided to try to precipitate the peroxide on filter paper.

A 5 percent solution of zirconyl chloride was made and #42 Whatman filter papers were placed in the solution and stirred for thirty seconds. The papers were then blotted and dried in

a 100° C. oven for 1½ minutes and then completely air dried. If dried too long in the oven, the papers turned brown. Previously 3, 5, 7, 10, and 13 ppm. iodide solutions had been made up with potassium iodide. The dried papers were placed in a 3 percent hydrogen peroxide solution, removed, and washed three times by swirling with water in a beaker. The wet papers were then folded and placed inside a plastic screen cone which was in a glass funnel. Twenty milliliter portions of the previously prepared iodide solutions were filtered through papers prepared in the above manner, and light yellow iodine solutions were obtained. One milliliter of cadmium iodide-linear starch reagent was added to the iodine filtrates, and gave blue colors of a gradually increasing intensity corresponding to an increase in the concentrations of the iodide solutions used. It was found that if distilled water was used as a blank run, a faint blue color developed in 10 minutes after the indicator had been added. If the papers were dried after the hydrogen peroxide solution treatment, and a water blank passed through, addition of cadmium iodide-linear starch gave a dark blue color. This showed the zirconium peroxide adhered to the paper much better when the wet method was used. Paper treated by the wet method did not oxidize a bromide solution. It was found that if a thorium nitrate solution was used instead of the zirconyl chloride solution, a colored blank was obtained. It was assumed that the thorium peroxide was not bound tightly to the paper and washed off when the solution was filtered. For this reason, the zirconium

peroxide paper was used for further study.

Zirconium peroxide papers were made, using the method mentioned previously, with 5 and 10 percent solutions of zirconyl chloride octahydrate. Three, 5, 7, 10, and 13 ppm. iodide solutions were passed through the papers and the filtrates collected. The optical densities of the solutions were read with the spectrophotometer at 615 millimicrons, one minute after adding the indicator. It was noted that there was no appreciable difference in the readings for the different papers made from the 5 and 10 percent zirconyl chloride solutions, so the 5 percent solution was used in further study. When 3 and 1 percent zirconyl chloride solutions were used, it was found that the optical densities fell off with an increase in concentration, indicating the amount of zirconium peroxide formed on the paper, was insufficient and had been exhausted.

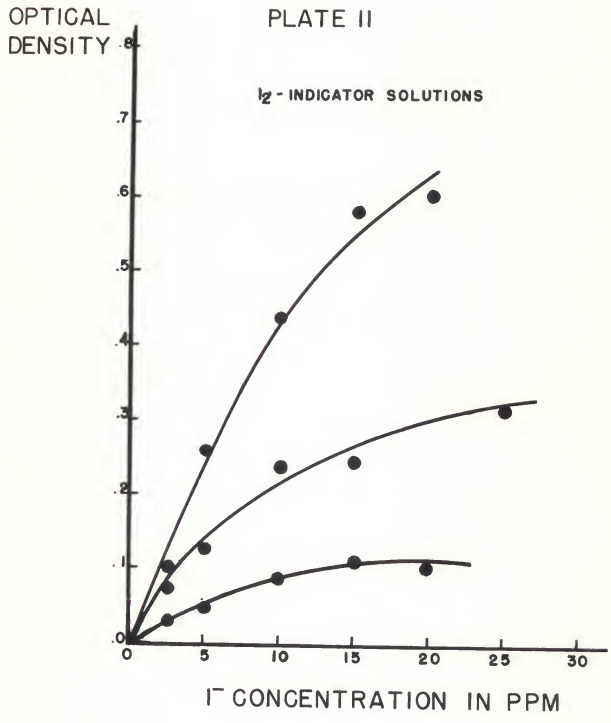
Various iodide solutions were made up and passed through the prepared paper. One milliliter of cadmium iodide-linear starch reagent was added to each sample and the optical densities read at 615 millimicrons, one minute after the addition of the indicator. The results of several runs are given on the graph shown (Plate II). A straight line relationship was obtained when the optical density was plotted versus the iodide concentration. The readings showed quite a wide variance, and the cause of this was investigated.

Five, ten, and fifteen ppm. iodide solutions were run through the zirconium peroxide paper and the optical densities read versus

EXPLANATION OF PLATE II

Optical densities of iodine solutions with starch indicator added.

PLATE II


OPTICAL DENSITY
.8
.7
.6
.5
.4
.3
.2
.1
0
I2 - INDICATOR SOLUTIONS
0
5
10
15
20
25
30
I⁻ CONCENTRATION IN PPM

time, after the indicator was added. The curves shown (Plate III) were obtained. These curves showed the optical densities increased with time and showed a blooming effect. The change was found to be most rapid, the lower the iodide concentration became.

As a further check, this process was repeated with the exception that the indicator was not added. Instead, a crystal of potassium iodide was added and the optical density of the resulting yellow I_3^- solution read on the spectrophotometer at 352 millimicrons. The curves shown (Plate IV) were obtained. They showed the blooming effect also, but in a different fashion. In the case of these solutions, the most rapid change occurred in the higher concentrations.

Both measurements showed the time of reading to be a factor. It was assumed that the blooming was due to a small amount of zirconium peroxide which came from the paper. Determinations were made in which the filtrate from the zirconium peroxide paper was refiltered through a barium sulfate mat. This did not affect the blooming; therefore, the cause was due to something in solution. The time of rinsing in water of the zirconium peroxide paper, after the hydrogen peroxide treatment, was varied from one to five minutes. It was found that the rinsing time had no effect on the blooming rate of the blue color. Hydrochloric acid and phosphoric acid were added to the filtrates in an effort to check the blooming. In the case of the hydrochloric acid, when added to a 10 ppm. iodide filtrate

EXPLANATION OF PLATE III

Blooming effect of iodine solutions with starch indicator added.

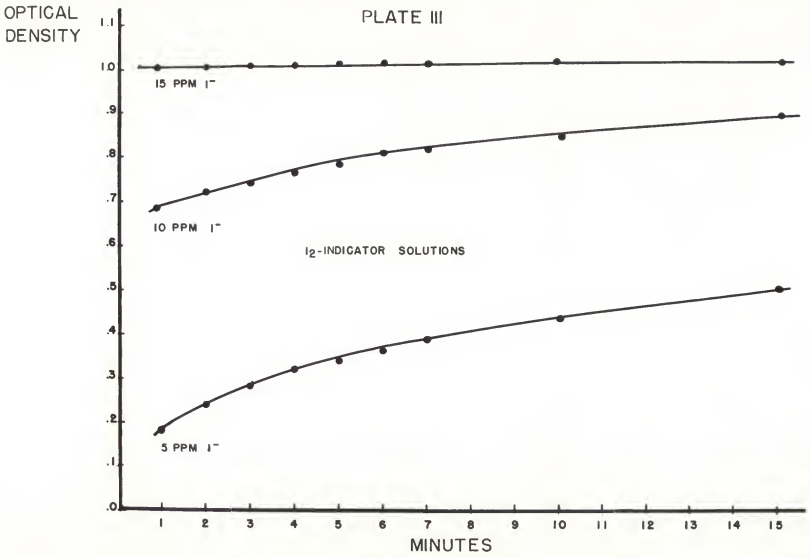
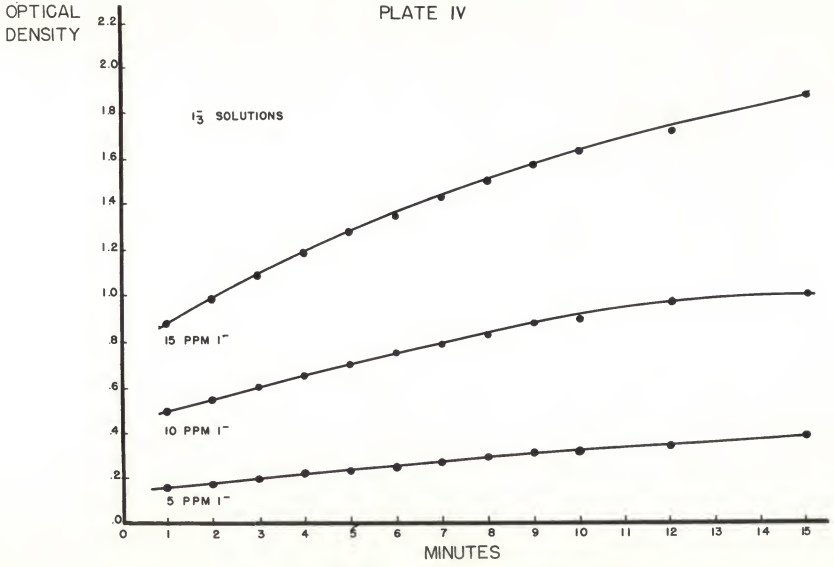


PLATE III
OPTICAL DENSITY
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
.0
15 PPM I⁻
10 PPM I⁻
I2-INDICATOR SOLUTIONS
5 PPM I⁻
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
MINUTES

EXPLANATION OF PLATE IV

Blooming effect of I_3^- solutions read without indicator.

PLATE IV


OPTICAL DENSITY
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
0
1/3 SOLUTIONS
15 PPM I⁻
10 PPM I⁻
5 PPM I⁻
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
MINUTES

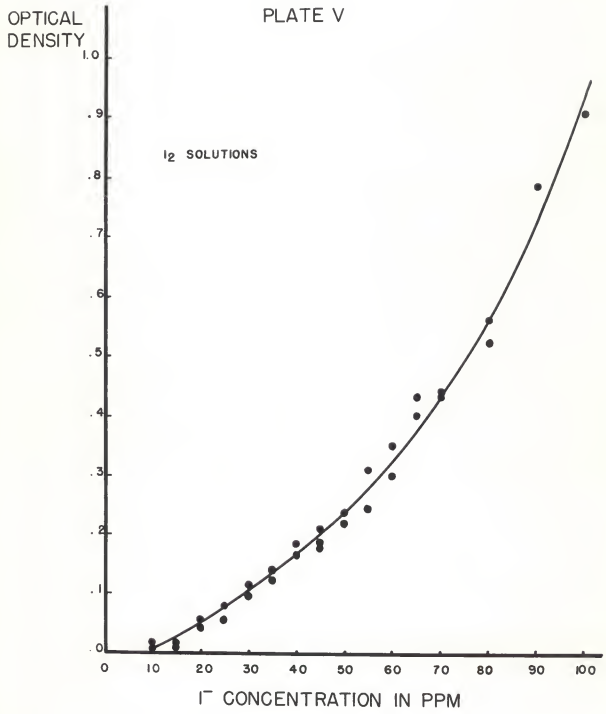
with indicator, the optical density values were lowered, but the blooming rate was not affected. When hydrochloric acid was added to a filtrate with a crystal of potassium iodide, the resulting I_3^- solution bloomed very rapidly. When phosphoric acid was added to a 10 ppm. iodide filtrate with the indicator, the usual blooming curve (Plate III) became a straight line; however the rate of blooming was much the same. It was found that potassium ferricyanide, formic acid, or the cobaltic ion had no effect on the blooming rate of the solutions.

During one of the determinations, it was noticed that iodine had sublimed from the solutions as they were being read on the spectrophotometer. To alleviate this, the iodine solutions were placed in an ice bath until the optical density readings were taken. Several runs were made with various concentrations of iodide solutions. The paper used was made by the wet method previously discussed. The iodine filtrates obtained were placed in an ice bath and the optical densities of the yellow solutions read directly at a wavelength of 350 millimicrons. Silica cells were used and were rinsed with carbon tetrachloride and water between readings. Iodide solutions ranging in concentrations from 10 to 100 ppm. were used. Several sets of zirconium peroxide papers were made and used in the determinations. From the curve (Plate V) it was noted that more consistant readings were obtained using the cold iodine solutions. The lower portion of the curve gave better results, as its slope is smaller. Graphing the results on semilog paper did not give a straight line.

EXPLANATION OF PLATE V

Optical densities of cold I_3^- solutions without indicator.

PLATE V


OPTICAL DENSITY
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
I2 SOLUTIONS
0
10
20
30
40
50
60
70
80
90
100
I⁻ CONCENTRATION IN PPM

It was found that as long as the solutions remained cold, the blooming was retarded.

Several similar runs were made and the indicator was added to the iodine filtrates. The iodine solutions were kept in an ice bath and the readings were taken one minute after the addition of the indicator. A straight line was obtained as shown in the graph (Plate VI). The maximum concentration used was a 20 ppm. iodide solution. Results could be duplicated easily with as low an iodide concentration as .5 ppm.. If the samples were allowed to become warm, the blooming was not quenched.

The results obtained by this method gave a maximum variance of .8 ppm. for a given iodide concentration. The most variance occurred with the higher concentrations.

The latter two methods could be used to determine the concentration of an unknown iodide solution. More accurate results were obtained using the indicator. With this method, higher concentrations would have to be measured by the method of aliquot portions. Care must be taken that the solutions are cold and the readings made at the same time interval after addition of the indicator.

Interference tests were run on the zirconium peroxide papers using 500 ppm. solutions of ions such as sulfate, carbonate, magnesium, fluoride, ammonium, and chloride, which are commonly found in water solutions. There was no interference from the ions that were studied. Acid solutions destroy the zirconium peroxide on the paper and cannot be used. If natural waters are

EXPLANATION OF PLATE VI

Optical densities of cold iodine solutions with starch indicator added.

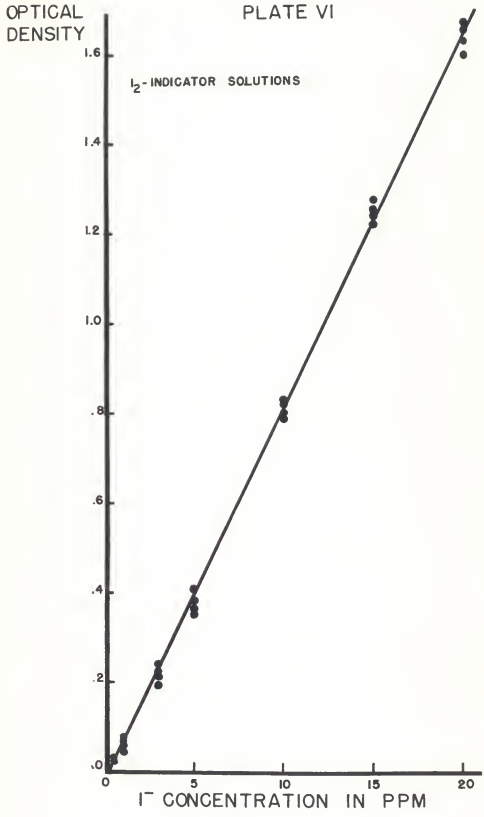


PLATE VI
OPTICAL DENSITY
I_2-INDICATOR SOLUTIONS
1.6
1.4
1.2
1.0
.8
.6
.4
.2
.0
0
5
10
15
20
I^- CONCENTRATION IN PPM

to be analyzed, they must be cleared of all organic matter as it causes the reduction of the iodine solutions.

Spot Test Paper

In the previous determinations, it was found that the zirconium peroxide paper would readily oxidize iodide solutions. It suggested that if the starch indicator were also on the paper, the presence of the iodide ion would be shown. Zirconium peroxide paper was made up by the method previously discussed. Various 1 percent starch solutions were made with crude A fraction corn starch, crude A fraction potato starch, pure A fraction potato starch, potato starch, and commercial "Faultless" starch. Zirconium peroxide papers were dipped in each of the starch solutions, blotted, and dried in air. Iodide solutions of 100, 15, and 1 ppm. concentrations were dropped on the papers and the results compared. All of the papers gave a blue ring with the 15 ppm. solution. The crude A fraction potato starch, and pure A fraction potato starch papers gave the most intense blue colors. The crude A fraction corn starch and "Faultless" starch papers gave less intense blue colors. It was decided that the crude A fraction potato starch should be used for further study.

It was necessary to find the best method for applying the starch to the paper. Three methods were tried. The dry zirconium peroxide paper was dipped in a 1 percent solution of the starch, blotted, and air dried. The filter paper was dipped in

the starch solution and air dried. The paper was then placed in a 5 percent zirconyl chloride solution for thirty seconds, blotted, and rinsed in a 3 percent hydrogen peroxide solution and again air dried. This method was the same as the second except the starch paper was rinsed in a 1:1 solution of 10 percent zirconyl chloride and 6 percent hydrogen peroxide, blotted, and air dried. The dried papers were tested with a 10 ppm. iodide solution, and those made by the first method were found to give the most intense blue color.

It was found that if a 15 percent solution of zirconyl chloride octahydrate were used in preparing the paper, a more sensitive test would result. When this paper was soaked in a 1 percent solution of the starch for thirty seconds, blotted, and air dried, it gave a faint blue ring with two drops of a 2 ppm. iodide solution. For practical use, a range of 5 ppm. iodide ion or greater should be used. With very dilute iodide solutions, the blue ring disappeared as the spot dried; however in more concentrated solutions, the colored spot was retained after it had dried. The zirconium peroxide starch paper gave a color ranging from a pale blue to black, depending on the concentration of the iodide solution. Paper made by the latter method was active after seven months, but somewhat less sensitive in action.

Paper made in the same manner using thorium nitrate solution instead of the zirconyl chloride solution, gave a test comparable to that of the zirconium peroxide paper. The thorium

peroxide starch paper would not give a blue spot with a bromide solution.

Active Starch

Since starch granules give a blue color in the presence of iodine, it suggests that if an oxidizing agent could be applied to the starch, it would serve as a qualitative material to test for the presence of the iodide ion.

Five grams of granular potato starch were placed in 50 milliliters of 5 percent zirconyl chloride solution, and the mixture stirred for one minute. The starch was filtered, placed in 50 milliliters of 5 percent zirconyl chloride solution, and the mixture stirred for one minute. The starch was filtered, placed in 50 milliliters of 3 percent hydrogen peroxide for one minute, filtered, washed, and air dried. One-half gram portions of the dried starch were placed in test tubes with various concentrations of iodide solutions. The treated starch gave a color down to 2.5 ppm. iodide concentration. The colors ranged from a light pink to a dark purple. It was found that colors could be duplicated consistantly with a given amount of the treated starch and a particular iodide concentration.

Different portions of starch were prepared by the above method using 5, 10, and 15 percent solutions of zirconyl chloride, and the activities of the prepared starches compared. The different starches gave colors of approximately the same intensity. The 15 percent zirconium starch took up the color faster than

the starch treated with the 5 and 10 percent zirconyl chloride solutions. It was decided that the 10 percent solution would be used in the preparation for further study since it was sufficient for the concentrations of iodide ion that could be used in this method.

A procedure for the preparation of the starch was standardized. Thirty grams of the starch were placed in 200 milliliters of a 10 percent zirconyl chloride solution and stirred for two minutes. The treated starch was filtered and washed with water. It was then placed in 200 milliliters of 3 percent hydrogen peroxide and stirred for three minutes. The starch was filtered, washed, and partially dried with suction and finally air dried. A small amount of this starch, 0.7 grams, was placed in a test tube with 10 milliliters of 20 ppm. iodide solution, and the mixture was shaken. A blue color appeared on the starch granules which reached a maximum intensity in 8-10 minutes.

Several types of starches were treated and their activities compared. General Chemical Co. potato starch, code 2351, Fisher Scientific Co. potato starch, no. S-513, and Fisher C.P. potato starch, were each prepared by the above procedure. The activities of the starches were compared by the above procedure. The activities of the starches were compared by placing 0.7 gram of each in a test tube with 10 milliliters of a 20 ppm. iodide solution and then shaking the mixtures. It was found that the first and last mentioned starches gave the most intense colors. After several hours, the starches began to lose their color due to

rupture of the granules. The C.P. starch gave a faint pink color with a 2 ppm. iodide solution. The C.P. starch gave the truest blue color and was used for further study.

The C.P. treated starch was tested for reproducibility of color by shaking three 0.7 gram portions in test tubes with 10 millliliters of 10 ppm. iodide solution. The three samples gave uniform colors and intensities. It was found that the starch colors could be best compared just after shaking, while the starch granules were suspended. Above a 75 ppm. iodide concentration, it was difficult to distinguish between different concentrations of iodide solutions.

It was possible to find the concentration of an unknown iodide solution by bracketing its resulting starch color between two known concentrations. Concentration differences of 5 ppm. could be determined readily. The useful range of the treated starch varies with the ability of a person to distinguish between closely related colors. An iodide concentration range of 5 to 75 ppm. would be practical for starch prepared by the above method.

The prepared starch was still active after seven months, but not quite as sensitive as when first prepared. For quantitative work, all of the starch used should be from the same preparation to insure reproducibility.

Some of the C.P. starch was treated with a 10 percent thorium nitrate solution and hydrogen peroxide, as in the foregoing preparation. It had an activity comparable to the zirconium

peroxide starch. Neither of the zirconium or thorium starches would oxidize a bromide solution.

During the course of the preceding work, various attempts were made to precipitate zirconium peroxide on other materials. Cotton, asbestos, and alumina, were treated in a fashion similar to the starch granules. The zirconium peroxide adhered well to the cotton and alumina after they were dried. The alumina was strongly active after two months storage at room temperature.

SUMMARY

The peroxides of several metals were prepared by homogenous precipitation. By using this method, the slimy precipitates reported by earlier investigators were avoided. The precipitated peroxides formed in discrete particles and were easily filtered.

A quantitative method for determining the iodide concentration of a solution was developed using paper on which zirconium peroxide had been precipitated. The paper oxidized an iodide solution to iodine, which was determined by a spectrophotometer.

A qualitative spot test for the iodide ion was developed using paper treated with zirconium peroxide and starch. Concentrations of iodide ion from 5 ppm. up, would give a color with the paper.

A qualitative and quantitative test for iodide ion was developed using granular starch on which zirconium peroxide had been precipitated. Differences in solution concentrations of 5 ppm. iodide could be readily determined.

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A STUDY OF CERTAIN METAL PEROXIDES AND THEIR APPLICATIONS IN IODOMETRIC ANALYSES

by

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Early investigators of some of the more uncommon metal peroxides were hampered in their work by the nature of the peroxides they were able to prepare. The peroxides were precipitated from a hydrogen peroxide solution by addition of a base. The resulting slimy hydrated precipitates were difficult to study.

In this thesis, the metal peroxides were prepared by homogeneous precipitation. Peroxides of zirconium, thorium, titanium, tin, uranium, and cadmium were prepared in this manner. The general method of preparation was simple and gave a good yield. A solution of the metal salt, hydrogen peroxide, and urea was placed in a three-neck flask and boiled with stirring. As the urea slowly decomposed and raised the pH of the solution, the peroxide of the metal precipitated in a granular form which was filtered, washed, and dried in an oven. The peroxides were examined by x-ray diffraction and found to be both crystalline and amorphous in structure. Analysis of the zirconium and thorium peroxides showed a composition corresponding to $Th_2O_7.4H_2O$ and $Zr_2O_5.3H_2O$. The peroxides of zirconium and thorium were very stable and were used in further studies. The zirconium and thorium peroxides readily oxidized iodide solutions; however, only thorium peroxide would oxidize a bromide solution.

One hundred mesh zirconium peroxide was placed in a glass column and iodide solutions were passed through it. Starch-iodide indicator was added to the resulting iodine solutions and the optical densities of the blue solutions were read on the Beckman spectrophotometer. It was found that the intensity of

the color increased when more concentrated iodide solutions were passed through the column. Results could not be duplicated in successive runs because the oxidizing power of the column gradually decreased.

When thorium peroxide was used in the column, similar results were obtained; the thorium peroxide column gradually lost its oxidizing power. Due to the hard and glassy nature of the peroxides, only the surface of the granules was involved in the oxidation reaction. This suggested that smaller sized particles would be more effective because of the larger surface they would have.

Zirconium peroxide was precipitated on filter paper and the treated paper placed in a funnel. Various concentrations of iodide solutions were passed through the treated papers and the filtrates placed in an ice bath. Starch-iodide indicator was added one minute before the solutions' optical densities were read on the spectrophotometer. A straight line relationship was shown when the optical densities were plotted versus iodide concentrations. Concentrations ranging from 0.5 to 20 ppm. iodide could be readily determined by this method.

When the optical densities of the yellow iodine filtrates were read directly, a range of 10 to 100 ppm. iodide gave a smooth curve when the optical densities were plotted versus concentrations. The first method using the indicator was the most accurate, but the method of aliquot portions would have to be used for high iodide concentrations.

When thorium peroxide was precipitated on filter paper, it was found that it did not adhere well to the paper. When the solutions were passed through the paper, the thorium peroxide was washed off into the solution.

When the filter paper on which zirconium peroxide had been precipitated was dipped in a 1 percent potato starch solution and dried, it made a convenient reagent which gave a spot test for the iodide ion. Iodide concentrations of 5 ppm. or greater gave a blue spot when dropped on the paper. The spot obtained with the lower iodide concentrations disappeared when it dried, but the colored spot obtained with the higher concentrated iodide solutions remained after the paper had completely dried.

A qualitative and quantitative reagent for the iodide ion was made by precipitating zirconium peroxide on potato starch granules. Dried starch treated in this manner became colored when shaken with an iodide solution in a test tube. The colors obtained ranged from pink to a very dark blue depending on the concentration of the iodide solution. Iodide concentrations ranging from 5 to 75 ppm. were easily compared in this manner and an unknown iodide concentration was determined by bracketing its color between the colors of two known concentrations. The colors obtained were best compared immediately after shaking while the starch granules were suspended in the solution.

During the previous work, it was found that zirconium peroxide could be precipitated on other materials such as cotton, and alumina, and that it adhered very well. The zirconium

peroxide paper, spot test paper, and zirconium peroxide starch were quite stable when prepared. After 7 months, the spot test paper and treated starch were still active and showed only a small decrease in sensitivity.