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# ANALYTICAL SEPARATIONS BY MEANS OF CONTROLLED HYDROLYTIC PRECIPITATION

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## ABSTRACT

To ascertain the completeness of precipitation of hydroxides under conditions of controlled alkalinity in the range pH 1 to 10, experiments were made with over forty of the chemical elements.

Discussion is given of possibilities for analytical separation through controlled hydrolytic precipitation.

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## I. INTRODUCTION

The advantages to be gained by controlling the alkalinity at which hydrolytic precipitations are made in analytical chemical operations do not appear to have been fully realized, nor have the possibilities for effecting separations thereby been sufficiently exploited. Experience in developing analytical procedures for the platinum metals and for dental gold alloys has indicated that much use can be made of the precipitation of hydroxides or hydrated oxides (the two terms are used interchangeably in this paper), if the precipitations are made under conditions of controlled alkalinity.

The control of alkalinity is easily accomplished with the aid of indicators, many of which are available today. Establishment of a definite end point may be attained with buffers or by merely neutralizing the solution with such reagents as sodium hydroxide, sodium carbonate, or sodium bicarbonate. The hydrolytic reaction itself serves to some extent as a buffer by liberating acid as the metal hydroxide is produced. Because of this the acidity of the solution tends to increase as the metal hydroxide is precipitated, so that slight adjustment is usually necessary to establish the final predetermined end point.

To illustrate the advantages of hydrolytic precipitation, consider a few familiar separations. The separation of copper from arsenic by means of polysulfide, for instance, is not sharp, and some copper sulfide tends to dissolve. Precipitation of hydrated copper oxide in a hot solution containing not more than 5 g of sodium hydroxide in 100 ml of solution is sometimes used to effect the separation of copper from arsenic. It is not necessary, however, to operate in a solution as strongly alkaline as this. The separation is easily accomplished if the solution is only as alkaline as pH 10. At this alkalinity a few minutes

of boiling suffices to complete the precipitation and coagulation of the hydrated copper oxide and to produce a precipitate which is easily filtered and washed.

In a similar manner copper is readily separated from selenium and tellurium. Lead likewise is conveniently separated from arsenic, selenium, and tellurium if it is oxidized to the quadrivalent state. In this case the lead separates quantitatively as hydrated dioxide at pH 10.

Tin likewise can be separated from copper without resort to the use of polysulfide. Chlorostannic acid hydrolyzes in acid solution and produces hydrated stannic oxide, precipitation of which is complete in the range pH 1 to 6. By operating at pH 1.5, an acidity far above that at which copper compounds hydrolyze, hydrated stannic oxide almost free from copper is produced. The small amount of adsorbed copper is completely eliminated by hydrolytically reprecipitating the tin from sulfuric acid solution at any acidity between 1 and 1.8 *N*.

Hydrolytic precipitations are also advantageous when dealing with the elements of the ammonium sulfide group. For instance, the separation of chromium from iron is usually accomplished by oxidizing trivalent chromium to chromate, and precipitating the iron as hydroxide. The reaction is customarily performed in fairly strong alkaline solution with the aid of sodium peroxide. A better way to effect the separation is to oxidize the chromium in hot, slightly acid solution by means of sodium bromate, and then to precipitate the iron by neutralizing the solution to pH 10. The conversion of trivalent chromium to chromate is rapid if the solution is slightly acid. Corrosion of the glassware, which occurs in strong alkaline solution, is avoided by operating at pH 10.

Not only iron can be thus separated from chromium but also cobalt, nickel, manganese, titanium, etc., as well as copper and lead. In the separation of aluminum from chromium, neutralization to pH 6.5 establishes the alkalinity most favorable to the minimum solubility of aluminum hydroxide.

In platinum metal analysis, hydrolytic precipitation furnishes the only accurate means of separating rhodium and iridium from platinum. It also enables one to recover osmium, ruthenium, and iridium for determination.

Hydrolytic precipitation is likewise valuable in isolating elements from solutions in which a considerable quantity of alkali salts have accumulated.

The idea of precipitation at definite acidity or alkalinity is not new. For example, Blum,<sup>1</sup> from observations made with a hydrogen electrode and with suitable indicators, found that the precipitation of aluminum hydroxide by ammonium hydroxide is complete in the range pH 6.5 to 7.5. These observations resulted in the specification of conditions suitable for the analytical precipitation of aluminum as hydroxide. The main purpose of the present paper is to direct the analyst's attention to the conditions of alkalinity which permit the quantitative hydrolytic precipitation of many of the metallic elements, and to point out how the hydrolytic method can be utilized in effecting chemical separations.

<sup>1</sup> William Blum, *J. Am. Chem. Soc.* **38**, 1282 (1916).

## II. HYDROLYTIC BEHAVIOR OF INDIVIDUAL ELEMENTS

To ascertain the completeness of precipitation of the various elements under conditions of controlled alkalinity, experiments with individual elements were made. It was found that the hydrated oxides of many of the metals were quantitatively precipitated within a rather narrow range of alkalinity. No attempt was made to follow the hydrolytic curves to locate the precise pH at which minimum solubility existed. Rather, the experiments were of an empirical nature, and the precipitations were made at definite alkalinities, dependent upon the indicators available.

In general, the experiments were performed as follows: Approximately 100 mg of an element was taken, in the form of one of its common salts. Precipitation was made by carefully neutralizing the boiling solution, 150 to 250 ml in volume, to a predetermined end point. The reagents used for neutralization were sodium hydroxide, sodium bicarbonate, or sodium carbonate. After 5 to 10 minutes of boiling, the final end point was reestablished, if necessary, and the precipitate was removed by filtration through quantitative paper. It is to be noted that ammonium hydroxide was not used. This reagent converts the compounds of certain metals, for example, those of cobalt, nickel, manganese, copper, and the platinum metals, into amines and not into insoluble hydroxides;

In most instances the filtrates were evaporated to dryness or concentrated to a small volume before subjecting them to test. The terms "quantitative precipitation" or "complete precipitation," as used in this paper, mean that the element in question either was not detected by sensitive tests or that its amount in the filtrate did not exceed 0.1 mg.

Since the direct addition of indicator to the solution was not always feasible, the following simple, convenient, and reliable method of determining the end point was used. The stirring rod was lifted so that its lower end was above the level of the solution in the beaker. A drop of a 0.01-percent solution of the indicator was allowed to run into the drop of liquid which clung to the rod. The end point so observed was for all practical purposes identical with that of the indicator placed in the main body of the solution. In this way there was no loss of material, such as is the case in the usual method of using an "outside indicator."

The indicators used in the experiments here described were sulfonphthalein indicators. In the form of their monosodium salts they are water soluble. These indicators and the color changes which occur on passing from acid to alkaline solution were: Thymol blue, which changes from red to orange at about pH 1.5, and from yellow to blue at about pH 10; brom phenol blue, which changes from yellow to blue at pH 4; brom cresol green, which changes from yellow to blue at pH 4.7; chlor phenol red, which changes from yellow to red at pH 6; brom cresol purple, which changes from yellow to blue at pH 6.3; brom thymol blue, which changes from yellow to blue at pH 7; cresol red, which changes from yellow to pink at about pH 8; and xylenol blue, which changes from yellow to blue at an alkalinity slightly greater than pH 8.

Although the color changes of these indicators may not correspond exactly to the true value of the hydrogen-ion concentration of the solution as measured by physical means, nevertheless, as the indicators have been used in these experiments, they do indicate the degree of alkalinity necessary to produce quantitative precipitation. The end points, therefore, are stated in terms of the indicators rather than in values of pH. It should be noted that both end points of thymol blue are utilized, the one at about pH 1.5 for the precipitation of stannic acid and the other for a great many of the other elements. To avoid unnecessary repetition, the end point of thymol blue without further designation means the one at about pH 10.

With most of the base metals it made little difference whether they were in the form of chloride, nitrate, or sulfate. In the case of those which form highly coordinated compounds, the platinum metals for instance, the nature of the attached acidic groups may influence their behavior on hydrolysis. A clear-cut example of this is the marked difference in behavior of the two compounds of ruthenium,  $\text{Na}_2[\text{RuCl}_6]$  and  $\text{Na}_2[\text{RuCl}_5\text{NO}]$ . The former hydrolyzes easily and completely in boiling solution at pH 6.3 to form hydrated ruthenium oxide. The latter produces no precipitate, since, apparently, these conditions are not sufficient to cause the splitting off of the tightly bound nitroso-group.

The hydrolysis of the platinum-metal complexes, as well as those of a number of other metals, is undoubtedly a stepwise process, and the resulting precipitate may contain acid groups. Furthermore, with the platinum metals and certain base metals, it makes no difference whether the reagent used to reduce the acidity of the solution is sodium hydroxide or sodium carbonate. In some instances, lead for example, the presence of carbonate is extremely important. In using the reagents, no attempt was made to exclude atmospheric carbon dioxide from the sodium hydroxide, nor atmospheric oxygen, since the object was to produce an insoluble precipitate and not one of some definite composition. Unless the analyst desires to prepare a compound of definite composition, it makes little difference to him whether the precipitate is a hydrated oxide or a basic salt, as long as it is completely insoluble at the alkalinities in which he is interested and does not contain the elements which he wishes to eliminate.

The observations on the individual elements which are here recorded were gathered largely in connection with problems arising in the analysis of platiniferous materials. Because of this, the precipitations of the individual elements were made in solutions which contained sodium nitrite or sodium bromate, both of which are used in systematic platinum-metal analysis. Except in a few instances, namely, the platinum metals, gold, lead, chromium, nickel, cobalt, and manganese, the recorded observations would be essentially those of the elements in the absence of nitrite or bromate. In those instances where these reagents influence the normal reaction, notation thereof is indicated. For convenience, the observations are grouped according to the arrangement of the elements in the periodic system.

## GROUP I

*Copper.*—Quantitative precipitation of bulky, flocculent, pale blue hydrated oxide occurs at the end point of cresol red or of xylenol blue.

At increased alkalinity the precipitate shrinks in size and turns dark brownish black. It is completely insoluble at the end point of thymol blue.

*Silver.*—If silver is taken as nitrate or sulfate, sodium hydroxide produces partial precipitation at an alkalinity slightly greater than that corresponding to the end point of xylenol blue. In the presence of nitrite there appears to be no precipitation in solutions less alkaline than the end point of thymol blue.

*Gold.*—When sodium hydroxide is added to a solution of chloroauric acid, no precipitation occurs in solutions less alkaline than the end point of thymol blue. The reducing action of nitrite causes the precipitation of metallic gold, which is complete when the acidity of the solution has been reduced to that of the end point of chlor phenol red.

## GROUP II

*Beryllium.*—There is no precipitation of beryllium hydroxide at the end point of brom phenol blue. Precipitation begins at about the end point of brom cresol green, and it is complete in the range from the end point of chlor phenol red to that of thymol blue.

*Magnesium, Calcium, Strontium, and Barium.*—At alkalinities up to that of the end point of thymol blue, precipitation of magnesium, calcium, strontium, and of barium is incomplete, even in the presence of carbonate.

*Zinc.*—Precipitation of hydrated zinc oxide is not quite complete at the end point of cresol red, but it is quantitative at the end point of thymol blue.

*Cadmium.*—Cadmium is possibly completely precipitated at the end point of cresol red or of xylenol blue, when carbonate is used. Precipitation is not quite complete at either the end point of brom cresol purple or of thymol blue, in the presence of sodium hydroxide or of carbonate.

*Mercury.*—Neither sodium hydroxide nor carbonate produces a precipitate in solutions of mercuric salts at alkalinities less than that of the end point of thymol blue. Precipitation does not begin to occur until the alkalinity greatly exceeds this end point.

## GROUP III

*Aluminum.*—The minimum alkalinity at which aluminum hydroxide is completely precipitated appears to be that of the end point of brom cresol purple. At alkalinities greater than pH 7.5 (about halfway between the end points of brom thymol blue and cresol red), aluminum hydroxide becomes increasingly more soluble.

*Gallium.*—Gallium hydroxide begins to precipitate at an acidity slightly higher than that which is required for indium. Precipitation of gallium is complete at the end point of brom phenol blue and at that of chlor phenol red. The precipitate is entirely redissolved at the end point of xylenol blue.

*Indium.*—Indium hydroxide begins to precipitate at an acidity slightly greater than that of the end point of brom phenol blue. It is quantitatively precipitated in the range between the end points of chlor phenol red and thymol blue.

*Thallium*.—No precipitation occurs with univalent thallium at alkalinities up to that of the end point of thymol blue. The presence of bromate causes incomplete precipitation of a dark-brown compound at the end point of cresol red.

*The Rare Earths*.—No experiments were made with the individual rare-earth elements. It is known, however, that quadrivalent cerium, like thorium, is completely precipitated hydrolytically at about pH 3. Precipitation of the trivalent members appears to begin at about pH 6 and, depending on the basicity of the individual oxides, the range extends to about pH 14, the alkalinity necessary to precipitate lanthanum.

#### GROUP IV

*Germanium*.—Solutions of germanium dioxide in hydrochloric acid give no evidence of precipitation in the range from tenth-normal acid to the end point of thymol blue. No precipitation appears to occur at even greater alkalinities.

*Tin*.—Quadrivalent tin is quantitatively precipitated in the form of hydrated stannic oxide from chlorostannic acid in the range from tenth-normal acid to the end point of brom cresol purple. When precipitated within this range of acidity, the hydrated stannic oxide is easily filterable. At alkalinities greater than that of the end point of brom thymol blue, the tin precipitate tends to become colloidal.

*Lead*.—There is no alkalinity at which the hydroxide of bivalent lead is completely insoluble. Precipitation of lead in the presence of carbonate is complete at the end point of xylenol blue.

In the presence of bromate, brown, hydrated lead dioxide is quantitatively precipitated in the range from the end point of brom cresol purple to that of thymol blue. The precipitate is most likely insoluble at even higher alkalinities.

*Titanium, Zirconium, Hafnium, and Thorium*.—No extensive experiments were made with this group of elements. Their salts tend to hydrolyze in acid solution. It was found that in the range studied, between the end points of brom cresol purple and thymol blue, titanium and thorium are completely precipitated, and presumably zirconium and hafnium are also.

#### GROUP V

*Phosphorus*.—This strongly acidic element participates in reactions in an anionic complex which forms precipitates with many metals, the solubilities of which depend on the degree of acidity or alkalinity of the solution. The alkali phosphates are soluble, but those formed with lead, for instance, are quantitatively precipitated between the end points of brom phenol blue and thymol blue, the range studied.

*Arsenic*.—Like the phosphates, arsenates produce precipitates with many metals. The alkali arsenates are soluble.

*Antimony*.—Antimony, which is more metallic than arsenic, forms a precipitate on reduction of acidity. Precipitation of a hydrated oxide, however, appears to be incomplete in the range of alkalinity studied.

*Bismuth.*—Precipitation of hydrated bismuth oxide is practically complete at the end point of brom cresol purple. Precipitation appeared to be complete at the end point of xylenol blue, when carbonate was present. When the alkalinity was increased to that of the end point of thymol blue, a small amount of bismuth was found in the filtrate.

*Vanadium.*—No precipitation occurs as acid solutions of sodium vanadate are gradually neutralized to and beyond the end point of thymol blue. Like arsenic and phosphorus, however, vanadium in the form of vanadate does produce precipitates with many metals.

*Columbium and Tantalum.*—No experiments were made with columbic and tantalum. Columbic and tantalum oxides precipitate in strongly acid solutions, and are insoluble at alkalinities less than that of the end point of thymol blue.

## GROUP VI

*Selenium and Tellurium.*—Over the range of alkalinity here considered, solutions of sodium selenate and of sodium tellurate gave no indication of the formation of precipitates. In common with the other oxyacid anions, selenates and tellurates do form precipitates with certain metals.

*Chromium.*—Characteristic trivalent chromium hydroxide is quantitatively precipitated at the end point of thymol blue, and possibly so at the end point of xylenol blue.

In slightly acid solution trivalent chromium is easily and completely oxidized by bromate to the chromate state. In this state of valency chromium is completely soluble over the range of alkalinity studied. Formation of insoluble chromates, which occurs when certain cations are present, will be discussed later. Nitrite, in slightly acid solution, reduces chromate to trivalent chromium.

*Molybdenum and Tungsten.*—No precipitation occurs in solutions which contain sodium molybdate or sodium tungstate. Here again, however, certain metals do form precipitates with the tungstate and molybdate radicals.

*Uranium.*—If uranyl nitrate is taken, complete precipitation of a yellow compound appears to be obtained at the end point of xylenol blue. The presence of carbonate causes incomplete precipitation.

## GROUP VII

*Manganese.*—Bivalent manganese is quantitatively precipitated at the end point of thymol blue, and possibly so at the end point of xylenol blue.

In the presence of bromate, brownish hydrated dioxide of manganese is quantitatively precipitated at the end point of xylenol blue.

*Rhenium.*—There was no evidence of precipitation as acid solutions containing perrhenate were gradually neutralized to the end point of thymol blue.

## GROUP VIII

*Iron.*—Precipitation of hydrated ferric oxide is quantitative from the end point of brom phenol blue to and beyond that of thymol

blue. Precipitation is likewise complete in solutions which contain nitrite.

*Cobalt.*—Bivalent cobalt is completely precipitated as a pale pink hydrated oxide at the end point of thymol blue.

The presence of bromate causes the quantitative precipitation, at the end point of xylenol blue, of a brownish, black hydrated oxide in which the valency of cobalt is probably three. This precipitate most likely remains insoluble at alkalinities greater than that of the end point of thymol blue.

Nitrite converts bivalent cobalt salts to nitrito-complexes. Complete decomposition of the nitrito-complex does not appear to be attained at the end point of cresol red, but it is at that of thymol blue. At this latter alkalinity the cobalt is quantitatively precipitated as a dirty-brown hydrated oxide.

*Nickel.*—Bivalent nickel is quantitatively precipitated as a pale-green gelatinous hydroxide at the end point of cresol red. It is likewise insoluble at the end point of thymol blue.

Bromate causes the formation of a black, well-coagulated hydrated oxide, precipitation of which is quantitative at the end point of cresol red. This precipitate, in which the nickel is most likely trivalent, is insoluble at the end point of thymol blue, and most likely so at even higher alkalinities.

Nitrite has no effect, since apparently the nitrito-complex of nickel is less stable than that formed by cobalt, and complete decomposition of it is readily attained.

*Ruthenium.*—In solutions containing ruthenium as a chlorosalt, but not as a nitrosochloride, well-coagulated hydrated oxide is completely precipitated at the end point of brom cresol purple, if the ruthenium is quadrivalent. If the ruthenium is trivalent, quantitative precipitation is likewise obtained, but the precipitate is more flocculent and settles less readily.

The effect of nitrite is to form a coordinated complex the sodium salt of which is soluble. Bromate causes the formation of volatile ruthenium tetroxide, especially if the solution is acid.

*Rhodium.*—Solutions containing trivalent rhodium precipitate yellow, flocculent hydrated oxide on neutralization. In slightly acid solution, bromate oxidizes rhodium, which is normally trivalent, to the quadrivalent state. Immediate neutralization precipitates well-coagulated olive-green hydrated dioxide completely at the end point of brom cresol purple, and the precipitate remains insoluble at the end point of xylenol blue and possibly at higher alkalinities.

Nitrite converts the chloroacids of rhodium to a nitrito-complex,  $[\text{Rh}(\text{NO}_2)_6]^{3-}$ . This complex is stable at alkalinities up to pH 12 to 14 and possibly greater.

*Palladium.*—Solutions containing bivalent palladium precipitate a brownish hydroxide on neutralization. Bromate oxidizes bivalent palladium to the quadrivalent state in slightly acid solution. Immediate neutralization precipitates well-coagulated, brown hydrated dioxide. Like that of rhodium, this precipitate is entirely insoluble at the end point of brom cresol purple and at that of xylenol blue.

Nitrite converts the chloroacid of palladium to a nitrito-complex,  $[\text{Pd}(\text{NO}_2)_4]^{2-}$ . This complex is stable at the end point of cresol red, but it begins to decompose as the alkalinity approaches that of the end point of thymol blue. At somewhat higher alkalinity it is

probably completely decomposed, with the precipitation of brown hydrated oxide.

*Osmium.*—In solutions containing quadrivalent osmium as chloro- or bromosalt, black hydrated osmium dioxide is completely precipitated hydrolytically in the range of acidity between the end point of thymol blue (in this case, pH 1.5) and that of brom cresol purple. The optimum acidity for analytical precipitation is that of the end point of brom phenol blue.

The effect of nitrite is to form a coordinated complex, the sodium salt of which is soluble. Bromate causes the formation of volatile osmium tetroxide, if the solution is acid.

*Iridium.*—As normally encountered, solutions of iridium in the form of its chloroacids contain both trivalent and quadrivalent iridium. For analytical purposes it is necessary to oxidize the iridium to a higher state of valency to insure complete precipitation on neutralization. The evidence appears to be that the precipitate produced when bromate is present contains the iridium in the hexivalent state. When bromate is added to the solution, the deep-green, almost black, precipitate which is formed is completely insoluble in the range between the end point of brom phenol blue and that of xylenol blue.

As in the case of rhodium and palladium, nitrite converts the chloroacids of iridium to a nitrito-complex,  $[\text{Ir}(\text{NO}_2)_6]^{3-}$ . This complex appears to have the same degree of stability as the corresponding rhodium one.

*Platinum.*—As normally encountered in solution, platinum is in the form of its chloro-compound,  $\text{H}_2[\text{PtCl}_6]$ .

In contradistinction to the chloro-complexes of palladium, rhodium, and iridium, that of platinum,  $[\text{PtCl}_6]^{2-}$ , hydrolyzes so slowly at the end point of brom cresol purple and at the concentration of platinum usually employed in analytical work that no precipitate appears; at least, the first stages of hydrolysis do not result in the formation of insoluble compounds. Given sufficient time, the chloroplatinate radical does behave in a manner similar to those of the other platinum metals. The effect of bromate appears to be to retard the hydrolysis which normally tends to occur.

Nitrite converts the chloroacid of platinum to a nitrito-complex,  $[\text{Pt}(\text{NO}_2)_6]^{2-}$ , whose stability is comparable to those of the nitrito-complexes of rhodium and iridium.

#### EFFECT OF FILTER-PAPER EXTRACT ON REPRECIPITATION

In those cases where repeated precipitation is made, special attention should be called to the influence which filter-paper extract has on the precipitation of certain elements when bromate is used. The disturbing effect is strikingly illustrated in the cases of cobalt and nickel. In the bivalent state nickel forms a gelatinous light-green hydrated oxide, and cobalt a pale-pink one. In the presence of bromate these metals are oxidized to a higher state of valency and precipitate as black, well-coagulated oxides. If such compounds are caught on filter paper, and the papers and oxides are digested in diluted hydrochloric acid, the resulting filtrates will contain organic matter. When the hydrated oxides of these metals are then reprecip-

itated in the presence of bromate, the black precipitates first formed change to those characteristic of the bivalent state. If, however, the filters and precipitates are decomposed and fumed with sulfuric and nitric acids, subsequent precipitation, with the addition of bromate, produces the oxidized black hydrated form of the oxides, and these remain stable.

### III. SEPARATIONS

It is not the intention here to outline the separation of each pair of elements, but only to indicate the applicability of the general idea of controlling the alkalinity of the solution in chemical separations.

Controlled hydrolytic precipitation has proved itself valuable in the development of analytical procedures for materials which contain the precious metals. The conversion of the four platinum metals, palladium, rhodium, iridium, and platinum, into their nitrito-complexes enables one to separate these four metals from a considerable number of other elements, merely by adjusting the alkalinity of the solution to that at which the particular element precipitates quantitatively. In general, the hydrated oxides of many of the base metals can be collectively precipitated, since the alkalinities at which they are completely insoluble practically coincide. This set of conditions, upon which a method was based for analyzing materials of the type of dental gold alloys<sup>2</sup>, has been successfully used in this laboratory to effect the separation of base metals in the analysis of native platinum.

Other papers<sup>3 4 5</sup> from this Bureau describe fully the precipitation of palladium, rhodium, and iridium as hydrated oxides, either singly or collectively, in their separation from platinum. These papers, as well as others,<sup>6 7 8 9</sup> also describe the hydrolytic precipitation of ruthenium, osmium, rhodium, and iridium for purposes of recovery from solution and of analytical determination.

When certain combinations of elements are in solution, reduction of the concentration of hydrogen ion causes precipitation of salts rather than of hydroxides. This situation occurs when anions of oxyacids are present. The precipitation of these salts is influenced by the degree of acidity or alkalinity of the solution, and in many instances there exist certain ranges of hydrogen-ion concentration over which particular compounds are completely insoluble. For example, lead phosphate was found to be quantitatively precipitated in the range studied, namely, pH 4 to 10. Similarly, lead chromate was found to be entirely insoluble in the range investigated, namely, pH 6.3 to 8. Lead carbonate was found to be insoluble at pH 8 when carbonate was present. Published data on solubilities give that of lead carbonate in water at room temperature as about 1 mg in 1 liter, and that of lead phosphate, as well as that of lead chromate, as about 0.1 mg. In the presence of common ions, these solubilities are undoubtedly still lower. Precipitation of such compounds finds an application in chemical separation, such, for example, as in separating lead from the platinum metals in nitrite solution.

<sup>2</sup> Raleigh Gilchrist, *J. Research NBS* **20**, 745 (1938) RP1103. \*

<sup>3</sup> R. Gilchrist, *BS J. Research* **12**, 291 (1934) RP655.

<sup>4</sup> R. Gilchrist and E. Wichers, *IX Congreso Int. quim. pura aplicada* **6**, 32 (1934).

<sup>5</sup> R. Gilchrist and E. Wichers, *J. Am. Chem. Soc.* **57**, 2565 (1935).

<sup>6</sup> R. Gilchrist, *BS J. Research* **3**, 993 (1929) RP125.

<sup>7</sup> R. Gilchrist, *BS J. Research* **6**, 421 (1931) RP286.

<sup>8</sup> R. Gilchrist, *BS J. Research* **9**, 547 (1932) RP489.

<sup>9</sup> R. Gilchrist, *BS J. Research* **12**, 283 (1934) RP654.

In many instances controlled hydrolytic precipitation effects the separation of those elements which form hydrated oxides from those which form oxyacids. For example, chromium, when oxidized to chromate by sodium bromate, is easily separated from copper, nickel, cobalt, manganese, titanium, aluminum, indium, or zinc, if the individual solution is neutralized to the particular end point of the metal in question. Collective separation is likewise possible, because many of the hydrated oxides are insoluble within the same range of alkalinity.

The separation of lead from elements which form oxyacids is interesting. As previously mentioned, lead is quantitatively precipitated by the chromate ion in the range pH 6.3 to 8. Under the influence of sodium bromate, lead chromate is decomposed when the alkalinity of the solution exceeds pH 7, and hydrated lead dioxide is precipitated. In a like manner, lead sulfate, which is appreciably soluble, is very readily decomposed, with the complete precipitation of hydrated lead dioxide. Similar separations of lead from selenate, tellurate, and arsenate take place. Preliminary experiments indicated that oxidation of lead and the production of lead dioxide resulted when lead phosphate, lead vanadate, and lead molybdate were treated with sodium bromate.

The ease with which the elements that form oxyacids are separated from other metals does not appear to be equal. Arsenic, selenium, and tellurium, in their highest states of valency, are readily separated from copper, for example, at an alkalinity of pH 8 to 10, without the addition of bromate. Vanadium, however, does not seem to be as easily separated; at least, at alkalinities less than pH 10. In all probability operation at a higher alkalinity would be more effective, but sufficient investigation was not made with vanadium to ascertain the necessary conditions.

In the presence of bromate, arsenic is separated from palladium, rhodium, and iridium. A separation of chromium from these three metals can also be effected, if bromate is added to the solution, but a better way is to remove the chromium as trivalent hydroxide in a solution in which the platinum metals have been converted to nitrito-complexes.

An interesting possibility for separation by hydrolytic precipitation appears to be that of copper and zinc from mercury. No precipitation occurs in solutions of mercuric salts which are not too concentrated until the alkalinity of the solution greatly exceeds pH 10. Experiments showed that hydrated zinc oxide and hydrated copper oxide, precipitated at the end point of thymol blue, were not contaminated with mercury. Other separations, which depend solely on differences in alkalinity, likewise can be made, such as that of stannic tin from copper, etc.; and it is most likely possible to effect the separation of germanium from gallium and indium, and of gallium from indium.

WASHINGTON, December 15, 1942.