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On the recovery of the nitrates of uranyl ion and silver (I) ion from laboratory residua

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ON THE RECOVERY OF THE NITRATES
OF URANYL ION AND SILVER(I) ION
FROM LABORATORY RESIDUA

by

Bruce Bertollette Hardman UC 1964
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Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY
UNION COLLEGE
MAY 1964



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This Thesis

Submitted by

Bruce B Hardman

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

JDPater

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The author wishes to express gratitude to Dr. William B. Martin and Prof. Robert W. Schaefer, of Union College, for their ideas relating to this project; and especially to Dr. Jermain D. Porter, of that institution, whose invaluable assistance, unending interest, and cooperation, made its completion possible.

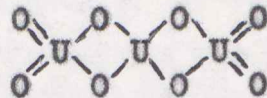
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PART ONE: ON THE RECOVERY OF URANYL NITRATE

"One of the worlds greatest tragedies is the murder of a beautiful theory by a brutal gang of facts."

INTRODUCTION

Uranium became known in the same epoch of history that saw the discovery of the planet Uranus. It was so named. Uranium is a rather active element and never occurs free in nature. Its ores include uraninite, carnotite, tyuyamunite, torbernite, and autunite. Of these, uraninite is by far the most important. This ore is sometimes called pitchblende and has a simplest empirical formula of UO_2 . Due to the fact that it is always found partially oxidized its composition may range between that of UO_2 and U_3O_8 . This latter form contains both tetra and hexavalent uranium. An illustrative structure is given below. It is sometimes regarded as uranyl uranate, which takes the formula $(UO_2)_2UO_4$. Perhaps the best proposed formula is $UO_2 \cdot 2UO_3$ (11).



Possibly the most striking property of this element is the fact that it is radioactive. The isotopes Pb^{206} and Pb^{207} result from the nuclear breakdown of U^{238} and U^{235} respectively. During the breakdown, ionized helium atoms (alpha particles) are one form of radiation emitted. Helium is always found in uraninite. It was in this material that helium was first discovered on earth.

Many additional isotopes of uranium are recognized with atomic weights that vary from 227 to 240. The two already mentioned emit alpha particles having an energy greater than 4.00 MeV. Their half-lives both exceed 10^8 years.

Since all isotopes of the same element have the same atomic number, which is an index to the number of electrons that will surround the nucleus of each neutral atom, their chemical properties are expected to be the same. This is so observed.

Metallic uranium is quite reactive. It decomposes water and might spontaneously burn in air if in the form of a powder. A special case of the Goldschmidt Reaction is among the numerous methods for isolating the element. It will be the only method cited here. The thermite reaction is another special case. Aluminum is used as the reducing agent. The oxidizing agent can be any of the uranium oxides. As an example:



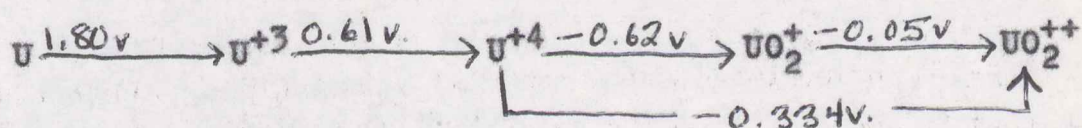
When uranium enters into chemical union with other elements two types of compounds are possible, namely, salts and non-salts. In the realm of binary compounds the salts are difficult to absolutely distinguish from the non-salts. These, however, are not the concern of this study. Within the category of salts formed by uranium, three oxidation states of the element are found: Uranium(III), uranium(IV), and uranium(VI). Uranium(III) salts are unstable for the most part. Uranium(IV) salts are derived from UO_2 acting as a basic anhydride. Uranium(VI) salts are derived from UO_3 , and since this oxide is amphoteric, fall into two classes- the uranates and the uranyl salts.

Uranates are produced when UO_3 undergoes salt formation with basic oxides. They have the general formula M_2UO_4 (where M is any monovalent positive species). The diuranates, $\text{M}_2\text{U}_2\text{O}_7$, however, are most frequently found.

Uranyl salts are produced when UO_3 undergoes salt formation with acids. In this process only one of the oxygen atoms is replaced by the acid radical per unit UO_3 . This results in the existence of the UO_2^{++} species, which is called the uranyl ion. These salts have the general formula UO_2X_2 (where X is any monovalent negative radical).

The following chart is given in the form of a resume.*

Oxidation-Reduction Potentials of Uranium Ions
(in 1 molar hydrochloric acid)



It shall be noted that the UO_2^+ ion will undergo disproportionation in aqueous solution to UO_2^{++} and U^{+4} . The existence of U^{+3} ions in solution is indicated by an intense red colour. This ion is water oxidized at a substantial rate. Solutions of U^{+4} are green and those of UO_2^{++} are green-yellow.

At this point an introduction has been given to the chemistry of uranium. Part One of this thesis is concerned with the recovery of uranyl nitrate from a laboratory residue. This residue is the result of an experiment in which the photolysis of uranyl oxalate is studied. The uranyl oxalate is formed by combining solutions of uranyl nitrate and oxalic acid. The following reaction occurs during photolysis.



Notice that the condition of the uranyl ion is not altered.

After photolysis, the remaining oxalate ion is detected by titration with permanganate ion in acid solution (sulphuric). The residue is obtained by precipitation from the resulting solution with ammonium hydroxide. Consequently, the chief impurity is manganese. The residue is believed to be in the form of hydrated oxides. The supernatant liquid contains other impurities in solution.

The recipe for the recovery follows. Part One will be concluded by a discussion of this procedure.

* From W. M. Latimer, Oxidation States of the Elements, Prentice-Hall, Inc., Second Edition (1952).

THE RECIPE

The recoverer shall take note of the following remarks:

- (a) As has already been mentioned, uranium is radioactive. Care must be taken throughout this procedure to prevent self-contamination. Overman and Clark have discussed the hazards involved (14). Radiation is not the only danger. If ingested, uranyl compounds are about as toxic as those of arsenic, the end result being slow emaciation (11).
 - (b) All waste materials that result from this procedure must be checked for radioactivity before being discarded. Radioactive wastes must be stored in a special container until a judgement be made as to the proper action. Do not pour such solutions down drains or place such solids in the crocks.
 - (c) Throughout this procedure use only reagent chemicals.
 - (d) Throughout this procedure use only clean apparatus. Both item (c) and item (d) are important for it would be a gross error to introduce additional impurities into a process designed to yield a pure product.
 - (e) Any apparatus used in this procedure should be so marked and not returned to the stock room until decontaminated.
 - (f) The author recom^mends reading the discussion of this procedure before making any crude attempts.
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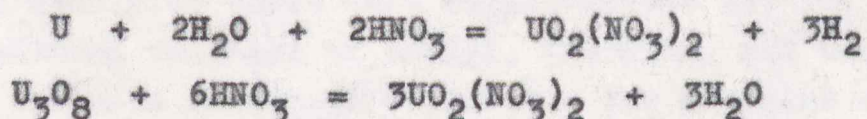
- I The amount of residue to be worked with is taken from the residue bottle and washed at least twice with hot distilled water. (A suction filtration is recom^mended.) The washed residue is then placed in a beaker such that the beaker is half full. The size of the beaker will depend upon the amount of residue involved. Concentrated nitric acid is then added making the beaker about $\frac{4}{5}$ full. This mixture is boiled carefully and under the hood until solution is effected (about 15 minutes). Any particles that remain undissolved are waste matter. The resulting solution shall be called "residue nitric solution" and is decanted and allowed to cool.
- II When cooled, concentrated ammonium hydroxide is added to the residue nitric solution until it is definitely basic. This will be made apparent by the formation of a yellow precipitate. When precipitation is complete, the solid matter is isolated by filtration and washed with distilled water at least twice. Although the solid will filter with difficulty, it must be so washed.

- III The yellow precipitate is then dissolved in a minimum amount of nitric acid. The resulting solution is made as nearly neutral as possible with ammonium hydroxide, without causing re-precipitation. If this should occur, go back to the second step or add nitric acid to just dissolve the solid. This solution is then placed in a *beaker* approximately twice the size of the original. It is diluted to approximately twice the original residue nitric solution volume, with a solution of ammonium carbonate, whose concentration is near but not in excess of 5 grams per 100 milliliters. This is a critical spot in the procedure and if a yellow precipitate forms too much of the carbonate is present. This precipitate must be replaced in the residue bottle. A white precipitate at this point might be expected and can be tolerated.
- IV The solution of step three is then warmed, but not boiled. Fifty degrees centigrade is recommended. A tenth molar solution of ammonium sulphide is then added drop-wise and in slight excess. A black precipitate may form. If no black precipitate forms a few drops of the sulphide are sufficient. The solution is allowed to stand for several hours. The supernatant liquid is then decanted. If a black precipitate formed it should be checked for the presence of uranium as instructed in the discussion. If uranium is there present, in sufficient quantity, the precipitate is returned to the residue bottle.
- V The solution of step four is boiled vigorously. This will cause the formation of a yellow precipitate. This solid is isolated by filtration and washed at least twice with distilled water. It is then dissolved in a minimum amount of nitric acid, diluted, and crystallization of the substances dissolved therein is forced.
- VI The crystals obtained from part five are then ground in a mortar with a pestle and dried for several hours in an oven at forty degrees centigrade. The temperature should not be allowed to rise above fifty degrees centigrade. The resulting powder is then boiled in 50 milliliters of diethyl ether for at least thirty minutes. This is best done under refluxing conditions. After the proper time lapse, the ethereal solution should have a yellow colour and white crystals should remain undissolved. If yellow crystals remain undissolved, decant the ethereal solution, and repeat the extraction upon the addition of more ether. When the extraction is complete, the ethereal solution is decanted and allowed to evaporate in the dark. The resulting powder is dissolved in distilled water. This solution should be an aqueous solution of uranyl nitrate. Crystallization is accomplished as many times as need be (twice if proper care has been taken) until the resulting crystals conform to the tests for reagent uranyl nitrate given in the American Chemical Society specifications. These are discussed later.

DISCUSSION

In short, this procedure is designed to separate uranium, in the form of uranyl ion, from manganese. Its success is dependent upon a chemical difference between the two species. This difference is exploited in step four of the recipe. Although this is the essential basis for the separation, the chemistry of the entire procedure merits discussion. An attempt will now be made to follow this chemistry and incorporate additional information pertaining thereto.

Step one involves dissolving the residue in nitric acid. The process employed is effective. Uranium and all its oxides will dissolve in this medium. The following equations are offered as illustrations (10).

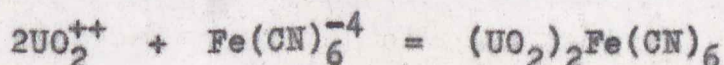


Lower manganese oxides also dissolve in this medium. It will be remembered that if this metal is present in the residue as such, the manganese species which immediately results is reduced in acid to the divalent form (15). The residue nitric solution thus contains both uranyl and manganous nitrates. This can be verified.

The presence of manganous ion is established by the sodium bismuthate test commonly employed in qualitative analysis. Since the residue nitric solution is acidic, the addition of a small lump of sodium bismuthate to a few milliliters of solution will oxidize the manganous ions therein to permanganate, which allows their detection on the basis of colour. The following reaction is observed.

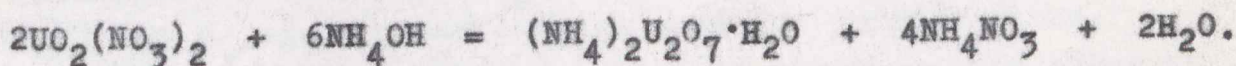


The presence of uranyl ion is indicated upon the addition of ferrocyanide ion to a different sample of solution. The following reaction is observed.



This test effectively overpowers the reaction of manganese ion with ferrocyanide to produce a white precipitate. Manganese does not interfere. Uranyl ferrocyanide is highly coloured and appears dark brown.

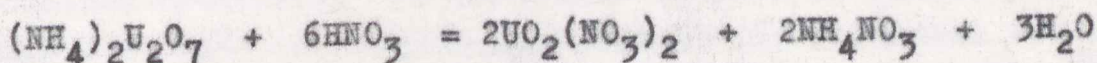
Upon the addition of an excess of ammonium hydroxide to the residue nitric solution, a yellow precipitate is produced. The reaction responsible is:



The yellow precipitate is ammonium diuranate. The fact that all metals form insoluble diuranates makes this reaction unable to effect a separation (15). Manganese diuranate is definitely precipitated to a considerable extent. Both of these solids are yellow.

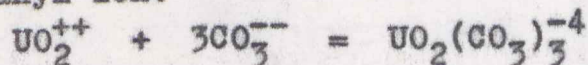
It is with step three that complications set in. Here, to a nearly neutral solution of uranyl, ammonium, and manganous nitrates, ammonium carbonate is added. The ammonium carbonate must be added in excess. If, however, the excess is "too excessive" the precipitation of ammonium uranyl carbonate will be noted. It is also yellow. The exact concentration of the carbonate ion necessary will depend upon the uranyl ion concentration and this is not predicted with ease.

The solution of ammonium, manganous, and uranyl nitrates was produced when the ammonium and manganous diuranates were dissolved in nitric acid. One such reaction is given below.



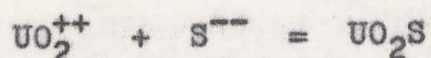
Manganous diuranate dissolves similarly.

The desired result from adding the ammonium carbonate is to complex the uranyl ion.

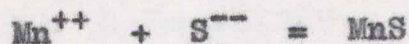


If the ammonium ion concentration is too great, the ammonium salt of this complex will precipitate (17). The figure, 5 grams of reagent per 100 milliliters of solution was given by Archibald(2) and Rodden(17) as being satisfactory. The author found it quite acceptable.

The following reaction will not occur upon the addition of ammonium sulphide to the above mentioned solution.



On the other hand, manganous ion is successfully removed under these conditions.



The precipitate is pink. Before this time (that is the addition of sulphide ion), any white precipitate present is basic manganous carbonate and/or hydroxide. If no ~~black~~ precipitate forms on standing, the latter has accomplished the purpose alone.

As already indicated, one sign of error at this stage is the precipitation of a yellow substance. If this is the case, the mixture should be boiled with vigor, the insoluble matter collected, and returned to the residue bottle. The instability of ammonium carbonate solutions is of prime concern. Care must be taken not to decompose excessive amounts during the procedure. If the concentration of carbonate ion is deficient from decomposition, UO_2S will also precipitate upon the addition of the sulphide. It is black. This can be detected by dissolving some of the precipitate in nitric acid, diluting, and adding ferrocyanide ion. Again, if this test is positive, the insoluble matter must be completely precipitated by boiling, collected, and returned to the residue bottle. More $(\text{NH}_4)_2\text{CO}_3$ should be added in the future if this occurred.

Should the separation be acceptable, and the chances of this are better than indicated by the previous discussion, the decanted solution containing the carbonate complex is boiled vigorously. This destroys the complex and permits the formation of the insoluble ammonium diuranate. When this precipitate is dissolved in nitric acid, the resulting solution contains uranyl, ammonium, nitrate, and hydronium ions. Consequently, when crystallization is forced, both uranyl and ammonium nitrates are produced. This may be verified by dissolving some of these crystals in water and treating with an excess of sodium hydroxide. The yellow precipitate formed upon this addition is sodium diuranate. The ammonium ion is detected by the odor of evolved ammonia gas or change in colour of moist litmus paper (the change is from red to blue) as the solution is heated.

The uranyl nitrate is isolated from the ammonium nitrate by solution in diethyl ether, for the latter will not dissolve therein. Before extraction, the impure crystals are pulverized

and dried. The purpose here is to remove any excess water not already locked in the crystal lattices of the hydrated salts. The uranyl nitrate hydrate (probably the hexahydrate) is efflorescent under the circumstances. Such excess wetness was found to inhibit the extraction.

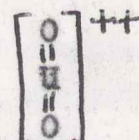
If for some reason the manganese separation was not effective and this went unchecked, the uranyl nitrate obtained after extraction will be impure with manganese due to the solubility of its nitrate in the ether. Ammonium nitrate will not dissolve in diethyl ether. It behaves as a typical amine salt.

Coordination complexes are known to form between metal electron acceptors (cations) and electron donating groups or ligands. Diethyl ether is such a group and both uranyl and manganous are such ions. The structure of the former is linear(5), as shown below. The ethereal

complex formed is reported as being of the following nature:

$UO_2(NO_3)_2 \cdot 2C_2H_5O$ (11). Ether is particularly convenient because

it may be boiled at a temperature below that at which uranyl nitrate begins to undergo its various decompositions. The "marked" solubility of $UO_2(NO_3)_2$ in diethyl ether has been pointed out by many, among whom is G. T. Seaborg (20).



The ethereal solution of uranyl nitrate that results is unstable in the presence of radiant energy (11) and the evaporation must be allowed to proceed in darkness, so the nitrate is not harmed in the process. The anhydrous form of the salt is not obtained from this evaporation. This is well established in that it has been reported the anhydrous form reacts violently with ether (11). No such reaction has been observed here. The resulting uranyl nitrate is re-crystallized to desired purity from water. The hexahydrate is obtained. As already mentioned, the tests for reagent purity of this salt are given in the American Chemical Society specifications (1). These will be discussed shortly.

Presently, however, some additional comments will be made.

The first of these concerns the condition of the ammonium hydroxide reagent used throughout the procedure to precipitate uranium as the diuranate. If this ammonium hydroxide is impure with carbonate or some other species that will cause the uranyl ion to complex, the precipitation of uranium will be incomplete. Oxalate and acetate are among these species. Others are given in the literature (9)(20).

The extraction into diethyl ether is done under refluxing conditions for two reasons. First, the volume of ether available to dissolve the uranyl nitrate must be maintained. Second, the possible existence of peroxides in the ether makes it dangerous to reduce the volume too much.

Uranyl salts have a characteristic yellow-green colour. This trait is also well displayed in aqueous solution. Uranyl nitrate exhibits a green fluorescence both in and out of solution.

When being crystallized, the nitric acid concentration of the solution from which crystallization takes place will determine the hydrate obtained. Three hydrates are possible- the di, tri, and hexa varieties. The latter is the most common. For a general rule, as the nitric acid concentration increases the number of hydrating water molecules per uranyl nitrate unit will decrease. At 75 grams HNO_3 per 100 grams of solution, for example, the dihydrate will form. The hexahydrate forms at concentrations which are considerably below 50 grams HNO_3 per 100 grams of solution. The recoverer will note, however, that during the final crystallizations, the nitric acid concentration is at a minimum.

Rodden has stated that uranium is usually determined more accurately by chemical than by radiochemical means (16). As a result, no radiochemical determinations were made. With regard to the former, uranium is best determined as U_3O_8 . This oxide is obtained by the ignition of ammonium diuranate. The procedure is described by Lundell and Hillebrand (9). It should be apparent that such calculations have no relevance here, for this recipe is not inefficient. There is no reason to suppose that substantial quantities of uranium are left behind. If this be the case, the recoverer becomes aware by testing unused precipitates with ferrocyanide as described earlier. If uranium is there present, the precipitates are returned to

the residue bottle. If the amount remaining is not significant they are discarded.

The requirements placed on reagent grade uranyl nitrate are to be found in the American Chemical Society specifications (1). The general tests will be briefly mentioned here. Any insoluble matter present is eliminated by the various crystallizations and therefore, none should be noted. Impurities of chloride and sulphate ion should not be noted due to the fact that neither of these species were introduced or precipitated in basic medium by ammonium hydroxide. Ammonium ion was eliminated by the ether extraction. Nevertheless, this must be tested for in the final product. The procedure is the same as that already given and no reaction to litmus should be noticed. Manganese must also be tested for. It may still remain in minute amounts if the sulphide precipitation was not carried out properly. Use the bismuthate test as directed. As a standard, a solution of manganous ion can be prepared by taking 0.1 milliliters of a fifty percent (by weight) solution of manganous nitrate, acidifying with HNO_3 and diluting to one liter. The uranyl nitrate should show a test less positive than this standard under the same conditions. It will be remembered that manganous nitrate is especially deliquescent and small amounts, therefore, can successfully be eliminated by the re-crystallizations. Furthermore, the sensitivity of the bismuthate test at such low concentrations is rather doubtful. The recoverer must suffer with this difficulty. The ideal result is to have no permanganate colouration given by bismuthate addition. The presence of other heavy metals or alkaline-alkaline earths was not noted by the author, when tested for according to the specifications. Some metals will interfere with the carbonate separation. Vanadium is one of these- others may be found in the literature (12)(17). These metals should not be present because they were never introduced. The same is true of iron (which does not so interfere). Other oxidation states of uranium (such as U^{+4}) must also be absent. The existence of such species

is most highly improbable due to the constant usage of nitric acid, which is easily reduced by them, they being oxidized to UO_2^{++} . In general, substances which will reduce permanganate should be absent. These can be detected with permanganate titrations. The acceptable limits for the tests are given in the reference (1).

The author is convinced that if the recoverer be in an analytical mood which is reflected in his work, this recipe will yield the desired result. On this note, Part One of the thesis will come to a close.

PART TWO: ON THE RECOVERY OF SILVER(I) NITRATE

INTRODUCTION

As a metal, silver has been known for thousands of years. The chemical symbol for the element is derived from its Latin name, argentum.

Not being particularly active, it is found in nature both as native silver and in a number of combined forms. Its ores include argentite (silver glance), stromeyerite, sylvanite, and polybasite. It is not especially abundant in nature and occurs percentage-wise by weight in the earth's crust to a lesser extent than uranium (20).

The chemical properties of silver greatly reflect its position in the electromotive series of metals. It is not attacked by non-oxidizing acids in the absence of air due to its inability to replace the hydrogen in them. It is, however, attacked, and thereby dissolved, by oxidizing acids such as nitric and sulphuric (the latter when hot and concentrated). The acid radical is reduced in the process.

Perhaps its most significant property, with regard to the opinion of the upper classes in the civilized world (they use it in ornamental objects because of its luster when polished) is its great affinity for sulphur. Silver combines with sulphur to form a black sulphide. This sulphide is affectionately named "silver tarnish". To the chemist, who regards this property

in a manner not nearly so trivial, it is of considerable importance. This statement will be reinforced by the discussion of the recipe which follows.

When in solution as silver(I) ion a number of complex ions are possible. It is known to form such ions with ammonia, cyanide, thiocyanate, thiosulphate, iodide, etc..

Silver compounds are sensitive to radiant energy, being decomposed to metallic silver in the presence of a suitable reducing agent. Silver nitrate, for example, will be reduced by sunlight in the presence of dust particles. Silver halides are especially sensitive. The chloride is decomposed by such energy liberating chlorine gas, in the absence of additional reducing agents. This fact has led to its occasional use in photography. Silver bromide is more commonly used because of its greater sensitivity.

Another outstanding property of silver metal is its ability to conduct electricity. Following a generally established connection, it is likewise a fine conductor of heat. Compounds of silver are also seen to be used in the field of electrochemistry, the silver-silver chloride reference cell being a specific example.

In the light of this brief introduction and an assumed general background, silver emerges as an important chemical material. It is consistently used in laboratories for one purpose or another. As a consequence of its relatively high cost, many efforts have been made to develop schemes for its recovery from residues in which it exists in unuseable form. The subject of Part Two of this thesis is another proposal. Account of other methods is given in the literature (2)(11)(15)(20). In specific, the residues with which this recipe is designed to deal were accumulated from various electrochemical experiments and related operations in a physical chemical laboratory for instruction purposes.

The recipe for the recovery follows. Part Two will be concluded by a discussion of this procedure.

THE RECIPE

The recoverer shall take note of the following remarks:

- (a) Silver compounds are poisons. The recoverer should be careful not to ingest these materials. Furthermore, compounds of silver will stain the skin by their reaction with various materials therein. This becomes important when one considers his personal appearance.
- (b) Upon reaction with various organic reagents, silver forms many substances which are violently explosive. The acetylide is one example. Also, on prolonged standing or boiling, the silver ammonia complex might be stimulated to undergo reactions which produce explosive substances. Do not boil such solutions or leave them standing over long periods of time.
- (c) Throughout this procedure use only reagent chemicals.
- (d) Throughout this procedure use only clean apparatus. Both item (c) and item (d) are important for it would be a gross error to introduce additional impurities into a process designed to yield a pure product.
- (e) The author recommends reading the discussion of this procedure before making any crude attempts.

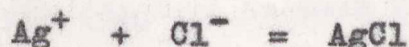
- I The amount of residue to be worked with is taken from the residue bottle and washed at least twice with distilled water. The washed residue is then placed in a beaker such that the beaker is nearly half full. It is then filled to working capacity with a solution of concentrated nitric and hydrochloric acids in equal volume amounts. This mixture is boiled under the hood until a definite coagulation of the solid material is noted. At this point the supernatant liquid is decanted and discarded. The solid is washed by filtration at least twice with distilled water.
- II The solid from step one is then placed in a beaker of the same size as the original. Enough concentrated nitric acid is added such that the volume of the mixture is twice that of the solid matter. This is now boiled under the hood for a few minutes. The supernatant liquid is decanted and discarded. The solid matter is washed by filtration at least twice with distilled water. It is then placed in another beaker the same size as the original. Distilled water is added making the beaker full to working capacity. This is boiled for several minutes. The supernatant liquid is decanted and a few drops of tenth molar chromate ion are introduced to the decantate. If a yellow precipitate forms follow step three. If this is not the case go on to step four.

- III If a yellow precipitate formed upon the addition of chromate ion in step two, wash the solid matter and repeat the boiling. Decant the supernatant liquid and again add chromate ion to it. If precipitation is noted a second time, repeat this step until it no longer persists.
- IV The solid matter remaining from step two (or step three) is washed at least twice with distilled water. It is then dissolved in a minimum amount of concentrated ammonium hydroxide. Once solution has been effected, dilute slightly, and decant the supernatant liquid. Discard any residual matter as it is waste. The supernatant liquid from earlier is then made acid with 6 molar HCl, which is added carefully and in excess. Do this under the hood. The precipitate is isolated by filtration and washed at least twice with distilled water.
- V The solid matter from step four is then dissolved in a saturated solution (or nearly so) of sodium thiosulphate. Use no more thiosulphate solution than necessary. Treat this solution with either of the following reagents: (a) enough distilled water to make the beaker slightly more than half full and half again as much formaldehyde solution (approx. 30%) (b) enough distilled water to make the beaker slightly more than half full and half again as much of a one molar solution of ammonium sulphide. The mixture is allowed to stand over night in the case of (a). Immediate precipitation should result in the case of (b).
- VI Once precipitation has occurred in step five, the solid material is isolated by filtration and washed at least twice with hot distilled water. It is then placed in a beaker such that the beaker is one third full. To this is added enough 20% nitric acid to make the beaker full to working capacity. The resulting reaction is allowed to proceed (heating gently if necessary). After reaction, the solution is boiled for a few minutes. Upon cooling, barium ion (from tenth molar barium nitrate) is added carefully, until precipitation is no longer noted. The mixture is stirred and allowed to stand for several hours.
- VII After standing, the mixture of step six is filtered and the insoluble matter is discarded. The filtrate is then made slightly basic with ammonium hydroxide. Formaldehyde solution (30%) is then introduced (5cc. for every 10cc. of solution). The resulting solution is then boiled ~~off~~ one hour in a proper sized beaker under the hood. The black precipitate that results is isolated and washed with boiling distilled water until the odor of formaldehyde can no longer be detected. The washed black precipitate is then dissolved in a minimum amount of nitric acid, the solution is diluted, boiled, and a crystallization performed. Crystallization is repeated until reagent silver nitrate is obtained therefrom.

DISCUSSION

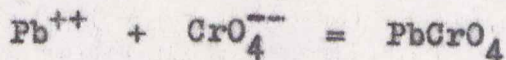
In essence, the first four steps of this procedure are aimed at separating silver from other materials that might be found in the residue. It is based on the chloride precipitation. There are, however, a number of materials that will interfere with this separation. Among them are all those cations whose chlorides are insoluble, namely, lead, palladium, mercury(I), copper(I), and thallium. In addition, anions that dissolve silver chloride, namely, cyanide and thiosulphate, will be bothersome. Furthermore, organic matter may prevent coagulation of the precipitate. The boiling in what is essentially aqua regia in step one combined with the subsequent boiling in nitric acid of step two, serves to eliminate the danger posed by all but lead (9). It will be noted that the presence of palladium and thallium in the residue is highly improbable and the possibility is thus neglected.

Any silver in the residue, no matter what its form, will be converted to silver halide by step one. Assuming the chloride:



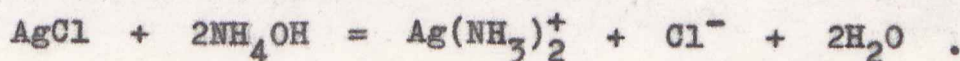
Silver chloride is not soluble in nitric acid. The actual purpose of step two is merely as a check on the effectiveness of step one in dissolving impurities. In both cases the supernatant liquid is discarded.

The elimination of lead in the first two steps is not complete (9). Its chloride, which is formed during step one, however, is appreciably soluble in hot water. Step three takes advantage of this point. After boiling, the supernatant liquid is decanted and chromate ion is introduced. The formation of yellow lead chromate indicates that lead chloride is present.

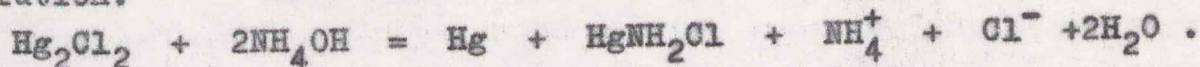


The step is repeated until no lead is found in the supernatant liquid, which indicates its removal from the solid material.

Once the removal of lead has been accomplished, the solid matter is dissolved in ammonium hydroxide. The following reaction occurs:

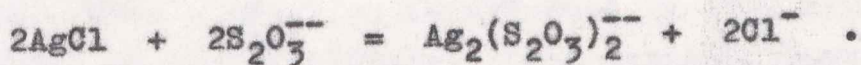


Silver is thereby placed in solution. Although impossible at this stage, mercury(I) could be prevented from going into solution:



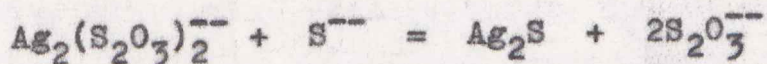
Furthermore, although highly improbable, any lead will be precipitated by ammonia as a basic white salt, which will be insoluble in excess reagent (8).

The re-precipitation of silver chloride is then effected. The precipitate should contain no other metal than silver. This is followed by dissolving the chloride in excess thiosulphate, which is obtained from sodium thiosulphate (incorrectly called "hypo" by the uninformed). The following solution reaction occurs:

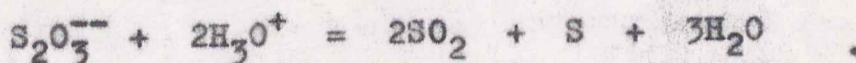


In actuality, the composition of the complex ion may not be as indicated, since this is greatly subject to the thiosulphate ion concentration. The above reaction, then, is just for representative purposes (20).

The thiosulphate complex is next converted to silver sulphide in step five. This can be done in either of two ways given (and these do not include all the possibilities). Method (b) involves the addition of ammonium sulphide to stimulate immediate precipitation.



Method (a) yields essentially the same product by introducing formaldehyde into the system. The exact happenings of the chemical change which results are not clear (at least to this investigator). It is possible that a number of reactions occur. For example, the formaldehyde (a reducing agent) may be oxidized to formic acid and cause the decomposition of the thiosulphate ions as follows:



This would leave free silver(I) ions to react accordingly,



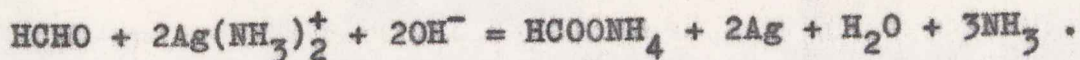
thereby causing a chain reaction involving the above chemical

changes. On the other hand, the formaldehyde could reduce the silver(I) ions directly to silver metal. If both possibilities are assumed, method (a) of step five would yield a mixture of silver and silver sulphide. If all the previous reactions occur, the precipitated silver metal may combine with the free sulphur in the system to produce the sulphide. In any event, when the black-brown precipitate is washed, silver has been freed from association with chloride ion, and this is an essential accomplishment.

Silver sulphide is the most insoluble known compound of silver, having a solubility product on the order of 10^{-51} (19). It does not dissolve in ammonium hydroxide and is not acted upon by radiant energy (11). It is, however, readily dissolved by nitric acid. Such a solution is effected in step six. The desired result is silver nitrate. Some complications set in. It seems that nitric acid will, in dissolving the sulphide, oxidize the sulphur to free sulphur, sulphate ions, etc.. This being the case, both silver nitrate and silver sulphate form, along with free sulphur and some gases in which sulphur is a component. Silver sulphate is relatively insoluble and will settle out of solution in small amounts. Boiling the mixture expels the gas species. The addition of barium ions (from barium nitrate) serves to precipitate any remaining sulphate as barium sulphate, which upon equilibration, due to its lesser solubility, will force the previously precipitated silver back into solution. At this stage barium and silver nitrates remain dissolved.

It is indeed interesting to note that the concentration of nitric acid used to dissolve the sulphide will determine the relative amount of silver nitrate and silver sulphate formed in the above solution process. Various researchers have reported that a 20% by weight solution of the acid yields the greatest amount of the nitrate- about 95% (11). The use of this concentration in the recipe is, therefore, highly recommended.

In step seven, the silver metal is precipitated from an ammoniacal solution of silver nitrate by formaldehyde. Barium ions are also present but are not so reduced. There is little question as to the equation for this reaction:



The nitrate ion undergoes no change. This silver precipitate will be black because all metals in the finely divided state appear thus. It is washed until the odor of formaldehyde is no longer detected.

One might suspect that mirroring could result from the previous reaction. This, however, is not generally the case and is most likely due to the fact that the system is boiled during precipitation. This boiling expells all gases the reaction produces. Some slight indication of mirroring might be noted depending upon the varying conditions, but this is not significant.

Silver metal is then dissolved in a minimum amount of nitric acid. The resulting solution is diluted and boiled to expell any gas products of the dissolving reaction. Crystallization is then accomplished. This is repeated as many times as need be to obtain the reagent grade salt. The exact specifications for this material are given by the American Chemical Society (1). These will presently be reviewed.

Any insoluble matter should be eliminated by the repeated crystallizations of the salt. Chloride ion and sulphate ion should not be present. The recipe does not allow these to remain as impurities if carried out correctly. Substances not precipitated by hydrochloric acid should also be absent, as the procedure is designed to remove them. The free acid content is the remaining problem. The author found that the re-crystallizations effectively removed it. In any event, the recoverer should make all the necessary tests as described in the reference, and make a judgement on the purity of the product accordingly.

Do not store the silver nitrate in open containers in the path of light, as it will be decomposed under such conditions as stated in the introduction to the recipe.

Any questions that the recoverer might have at this point, which can not be answered by this text, can be investigated in the literature. The bibliography provided hereafter is rather comprehensive. If the answers can not be so found, he might seek them in the laboratory. This should be especially rewarding indeed, if performed in the spirit of science.

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