Selected Studies of Organic Reagents.

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SELECTED STUDIES OF ORGANIC REAGENTS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Department of Chemistry

by

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B.S., Lebanon Valley College, 1939
M.A., University of North Carolina, 1941
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TABLE OF CONTENTS

CHAPTER                                PAGE

I  INTRODUCTION..............................................1

II THE SPOT TEST DETECTION OF ANTIMONY
   BY MEANS OF GOSSYPOL.................................2

III DETECTION OF VANADIUM BY MEANS OF
   SPOT TESTS...............................................9

IV A COMPARISON STUDY OF THE COPRECIPITATION
   OF CATIONS BY ORGANIC AND INORGANIC
   PRECIPITANTS..........................................19

V SUMMARY....................................................29

VI BIBLIOGRAPHY..............................................31

VII VITA.....................................................36
The use of organic reagents in analytical chemistry has become increasingly important in recent years. It was the aim of this research project to study some of the applications of several of these reagents as related to current problems. Two applications in spot tests and one of a more fundamental nature were investigated. The latter work consisted of a study of coprecipitation of cations by organic precipitants.

Spot Test for Antimony

A test for antimony has been developed based on the reaction between trivalent antimony and gossypol. The test is highly selective and is capable of detecting 0.5 microgram of antimony at a limiting concentration of 1 to 100,000.

The procedure in general is to first adjust the antimony solution to between 0.4 N to 0.7 N with respect to hydrochloric acid. One drop of this solution is added to a spot plate followed by one drop of a 1:4 phosphoric acid solution and four drops of a 0.1% acetone solution of gossypol. Antimony in the range of 0.5 to 10 μ per drop gave an orange to red precipitate. Greater than 10 μ per drop gave a distinct red precipitate.

Considering all of the requirements for a good spot test, gossypol appears to be superior to any other reagent for antimony which has been previously reported in the literature. It is sensitive, highly selective, stable and
readily available. The spot test procedure is very simple, requiring no elaborate conditioning treatments or specialized technics.

Spot Test for Vanadium

Two tests for detecting vanadium have been developed. They are based on the reaction of \( \alpha \)-benzoinoxime with vanadates and of \( \alpha,\beta \)-dipyridyl or ortho phenanthroline with ferrous iron. The latter is formed by the reduction of added ferric iron by vanadyl ion. The \( \alpha \)-benzoinoxime method is capable of detecting 1 microgram of vanadium at a limiting concentration of 1 to 50,000 and the \( \alpha,\beta \)-dipyridyl or ortho phenanthroline method is capable of detecting 0.1 microgram of vanadium at a limiting concentration of 1 to 500,000. The latter method is more sensitive than any test reported in the literature.

The \( \alpha \)-benzoinoxime procedure is carried out by placing one drop of the vanadate solution to be tested in a spot plate and to it is added one drop of \( \alpha \)-benzoinoxime reagent followed by one drop of 3 N sulfuric acid. A yellow precipitate indicates the presence of vanadium.

The \( \alpha,\beta \)-dipyridyl and ortho phenanthroline procedure is carried out by placing one drop of the vanadyl solution to be tested in a spot plate and to it is added one drop of each of the solution of ferric chloride, reagent and disodium phosphate. The presence of vanadium is indicated by a red solution with \( \alpha,\beta \)-dipyridyl and an orange solution with ortho phenanthroline.
Detailed interference studies were made on reported tests for detecting vanadium which use dimethylglyoxime-iron and sodium tungstate as reagents. Improvements were made in the dimethylglyoxime test by adding disodium phosphate which prevents the precipitation of a number of ammoniacal-insoluble ions and excess ferric iron which is added for the same purpose as described for \( \Delta,\Delta \)-dipyridyl. This greatly simplifies the interpretation of the results and makes it possible to carry out the test in a spot plate.

By using a combination of the methods studied it is possible to detect vanadium at extremely low concentrations and in the presence of over one hundred diverse ions at a concentration of one hundred times that of the vanadium.

Coprecipitation Studies

Studies were made on typical classes of organic-inorganic reactions concerning their tendencies to coprecipitate extraneous cations. In the case of cation precipitants simple normal salts, normal chelate salts, inner complex salts and polynuclear complex formations were studied. One anion precipitant was investigated which formed a simple normal salt type compound.

The findings indicate that organic precipitates in general coprecipitate cations to a greater extent than inorganic precipitates. The probable mechanism in such coprecipitation involves the formation of colloidal particles which flocculate under the influence of the electro-
lytes present in the immediate zone of reaction. Trivalent cations are reported to have very favorable flocculation values and as a consequence would be most liable to be carried down with the precipitate. The experimental data substantiate this as trivalent chromium and aluminum were found to be coprecipitated to the greatest extent.
INTRODUCTION

Two of the more important applications of organic compounds to analytical chemistry are in the spot test technic for detecting microquantities of inorganic ions and in gravimetric analysis. In general organic reagents have proven to be both sensitive and highly selective in detecting inorganic ions. This makes them especially useful in spot test work. In gravimetric analysis the use of organic reagents has developed rather slowly although a number of very useful procedures have been reported. This may be due to some extent to the lack of more fundamental studies on these reagents. An investigation of this nature was undertaken in which the coprecipitation of cations by organic precipitants was studied.

Three manuscripts have been prepared for publication. One of these describing the use of gossypol for the spot test detection of antimony has been accepted for publication by Analytical Chemistry. A second paper dealing with the spot test detection of vanadium has been submitted to Zeitschrift Für Analytische Chemie and a third paper dealing with coprecipitation studies of organic precipitants has been submitted to Analytica Chimica Acta. The three manuscripts as prepared for publication are presented in the dissertation.
THE SPOT TEST DETECTION OF
ANTIMONY BY MEANS OF GOSSYPOL

by
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A test for antimony has been developed based on the reaction between trivalent antimony and gossypol. The test is highly selective and is capable of detecting 0.5 microgram of antimony at a limiting concentration of 1 to 100,000.

A number of spot tests for antimony have been reported in the literature (10,4,8,7,9,12,5) but they often leave much to be desired due either to lack of specificity, poor sensitivity, instability or unavailability of the reagent, or a combination of these. The test which showed the most promise was based on the red color formed between trivalent antimony and 9-methyl-2,3,7-trihydroxy-6-fluorone. This test, as originally proposed by Wenger and Blancpain (12), lacked specificity but the changes in procedure recently reported by Gillis, Hoste, and Claeys (11) have overcome this objection to some extent. Despite the improvements in the procedure there remain several disadvantages: a number of ions still interfere, the reagent is not commercially available, the synthesis of the reagent is not satisfactory, and the solution of the reagent is not stable.
Boatner et al. (2) recently reported the use of antimony trichloride for the spectrophotometric determination of gossypol in cotton seed extract, based on the red color of chloroform solutions of the reaction product. The structure of the gossypol as reported by Adams and his co-workers (1) contains two aromatic ortho dihydroxy groupings. Proceeding from the gossypol-antimony trichloride spectrophotometric test and the aromatic ortho dihydroxy group action displayed toward antimony by such compounds as pyrocatechol, pyrogallol (7,9), and 9-methyl-2,3,7-trihydroxy-6-fluorone (12), an investigation was undertaken to study the use of gossypol as a spot test reagent for antimony.

Reagents

Gossypol Solution: purified gossypol obtained from the Southern Regional Laboratory, New Orleans, La., was made up to a strength of 0.1% in reagent grade acetone.

Phosphoric Acid Solution: one volume of 85% reagent grade phosphoric acid was diluted with four volumes of distilled water.

Experimental

The use of the spot plate as a medium for carrying out the test was found to be far superior to paper. The procedure followed in general was to adjust the antimony solution to between 0.4 N and 0.7 N with respect to hydrochloric acid and then add this solution to the spot plate followed by two drops of gossypol solution per aqueous test
drop. The evaluation of the test was made after thirty
seconds had elapsed. Antimony in the range of 0.5 to
10 μg per drop gave an orange to red precipitate.
Greater than 10 μg per drop gave a distinct red precipitate.

The determination of the limiting concentration and
limit of identification was performed in accordance with
the procedures described by Feigl (6). Interference
studies followed in general the procedure discussed by
West (13) except that the concentration of the antimony
ion in solution was 0.01% and that of the ions used in the
interference studies was 1%. Additional interference
studies were made against a control having a concentration
of antimony in solution of 0.002%. The interference
studies were carried out on solutions acidified with hydro-
chloric acid in order to duplicate test conditions.

The ions investigated in the interference studies are
given below in their more common forms. It is realized
that in many instances the ions concerned are present as
complexes, but where structures of such complexes may be
in doubt, only the valence of the central atom is indicated.

Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Ca²⁺, Cu²⁺, Ag⁺, AuCl₄⁻, Be²⁺, Mg²⁺,
Ca²⁺, Ba²⁺, Sr²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Hg²⁺, B(OH)₃⁻, B₄O₇⁻,
Al³⁺, Ga³⁺, In⁺⁺, La⁴⁺, Ce⁴⁺, Tl⁺, CO₃⁻, SiO₃⁻,
TI⁺⁺, Sn⁺⁺, Sn⁺⁺⁺, Pb⁺⁺, Zr⁴⁺⁺, Th⁴⁺⁺⁺, NH₄⁺, NO₂⁻,
NO₃⁻, H₂PO₄⁻, P₄O₁₀⁻⁻⁻⁻, HPO₄⁻⁻⁻⁻, P₂O₁₀⁻⁻⁻⁻, PO₃⁻,
HPO₄²⁻, P₂O₇⁻, VO₃⁻, HAsO₃⁻, HAsO₄²⁻, Sb⁵⁺⁺⁺, Bi⁷⁺⁺⁺,
Procedure

The solution to be tested must be acidic (0.4 N to 0.7 N with respect to hydrochloric acid) and should be gently warmed prior to making the spot test.

On a spot plate, place one drop of the test solution and to it add one drop of the phosphoric acid solution followed by four drops of the gossypol solution. An orange or red precipitate indicates the presence of antimony.

If the antimony in solution is in the pentavalent state it must be reduced to the trivalent form by means of sodium sulfite prior to carrying out the test.

Remarks

The gossypol reaction, when used as a spot test, has a limit of identification of 0.5 μg of antimony per drop of solution at a limiting concentration of 1 part in 100,000. No positive interferences were found when the interference tests were compared with controls containing 1 μg of antimony per drop. Vanadate, dichromate, iodate, bromate,
perosmic and molybdate ions give negative or masking interferences. The interfering action of the oxidizing agents is due to the formation of pentavalent antimony and/or the reaction of gossypol with the excess oxidizing agent. Molybdate, dichromate, vanadate and perosmic ions react with gossypol alone to form colored precipitates: molybdate-yellow, dichromate-brown, vanadate and perosmic-green. Iodate and bromate ions do not form colors with the reagent alone but in the presence of gossypol and antimony they cause the test color to be a faint green. Attempts to reduce these oxidizing agents in the presence of antimony in the spot plate were not satisfactory. The colors produced in these interfering reactions as well as the inherent colors of such ions as permanganate, chromous and various platinum metal complexes tend to complicate the interpretations of test results. The phosphoric acid used in the test prevents the interfering effects of ferric, tetravalent titanium, stannous, stannic and tungstate ions which would normally give the following colors with the reagent: ferric-green, tetravalent titanium and stannous - orange, stannic - red and tungstate - reddish brown. Zirconium, fluorides, thiosulfates, oxalates and tartrates are masking interferences but the interference due to fluoride can be removed successfully by the addition of boric acid which sequesters the fluoride as the tetrafluoroborate complex. Sulfide is not compatible with antimony. Nitrite ion oxidizes the trivalent antimony to the pentavalent state.
which does not form a colored product with gossypol. The excess nitrite ion can be removed by warming the acidic solution and then the pentavalent antimony can be reduced by the addition of sodium sulfite.

The acidity of the test should be controlled quite carefully. With hydrochloric acid concentrations below 0.4 N the antimony oxychloride begins to precipitate and above 0.7 N the color formation between the antimony and gossypol is suppressed.

Gossypol is reported to be unstable when stored at room temperature (3). In order to determine the effect of the decomposition of the gossypol on its use as a spot test reagent, the dry powder and an acetone solution of the material were stored in the dark at an average temperature of 80°F. At the end of four months the powder and the solution had darkened somewhat but both were satisfactory for use in the spot test.

Conclusion

Considering all of the requirements for a good spot test, gossypol appears to be superior to any other reagent for antimony which has been previously reported in the literature. It is sensitive, highly selective, stable and readily available. The spot test procedure is very simple, requiring no elaborate conditioning treatments or specialized technics.
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(7) Feigl, F., Mikrochemie, 1, 74 (1923).


Two new tests for vanadium are proposed using as reagents 2-benzoinoxime and either 2,2'-dipyridyl or ortho phenanthroline with ferric iron. Detailed interference studies have been made on reported methods which use as reagents sodium tungstate and dimethylglyoxime with ferric iron.

The detection of vanadium is of significance due to the growing importance of its use in steel and alloys. A number of spot tests for its detection have been reported (1,3,5,8,9,10,11,13) but no detailed interference studies or comparative data are available showing relative merits of the tests proposed. After careful consideration of the published methods two were selected for further study and development and additional investigations were made to determine the feasibility of developing new test procedures.

The tests selected for study were the procedure reported by Ashburn and Reedy (1) which depends on the intensification of the yellow color of slightly acidic solutions of vanadates by tungstate, and the procedure reported by Ephraim (3) which is an indirect method based
on the deep red color resulting from the reaction of ferrous iron and dimethylglyoxime in the presence of ammonia. The ferrous iron is formed when vanadyl ion reduces added ferric iron in the alkaline solution.

In the survey for new test procedures a study was made of various organic compounds that were reported to give colored products with vanadium. Knowles (7) observed that \( \alpha \)-benzoinoxime forms a precipitate with vanadates in mineral acid solution. Duke (2), in his studies of ammoniacal solutions of salicylaldehyde, found that precipitates were formed with divalent vanadium. Flagg and Furman (6) observed that salicylaldoxime forms a black precipitate with vanadates. Exploratory studies on the use of these organic compounds as spot test reagents for vanadium indicated that salicylaldehyde and salicylaldoxime were not acceptable due to poor sensitivity but that the \( \alpha \)-benzoinoxime showed considerable promise.

A research program was undertaken which consisted of a more detailed interference study of the sodium tungstate and dimethylglyoxime tests and of methods for improving the reported testing procedures. In addition, the possibility of developing new tests for vanadium using \( \alpha \)-benzoinoxime, \( \alpha \), \( \beta \)-dipyridyl and ortho phenanthroline were investigated.

General Discussion

The \( \alpha \)-benzoinoxime and tungstate methods give a positive test with vanadium when it is in the pentavalent state and
the methods which depend on the color formed between ferrous iron and \( \alpha,\alpha'- \text{dipyridyl} \), ortho phenanthroline and dimethylglyoxime give a positive test with vanadium in the quadrivalent state. Vanadium in its lower state of oxidation may be oxidized to form vanadates by the addition of an agent such as bromine with subsequent warming. The excess oxidant must be removed. This treatment will also eliminate reducing agents which might interfere. Vanadate compounds are readily reduced to vanadyl on heating with concentrated hydrochloric acid.

\[
\text{V}_2\text{O}_5 + 10\text{HCl} \rightarrow 2\text{VCl}_4 + 5\text{H}_2\text{O} + \text{Cl}_2
\]

Scope of Investigation

The spot plate was used as the medium for carrying out all of the investigations. The procedure followed for determining the limiting concentration and limit of identification was that described by Feigl (4). Interference studies followed in general the procedure discussed by West (14). The concentration of the ions investigated was one hundred times that of the vanadium used in the interference studies. These ions were present during the reduction of pentavalent vanadium to the quadrivalent state in the cases of the dimethylglyoxime, \( \alpha,\alpha' \)-dipyridyl and ortho phenanthroline tests.

The ions investigated in the interference studies are given below in their more common forms. It is realized that in many instances the ions concerned are present as
complexes, but where the structure of such complexes may be in doubt, only the valence of the central atom is indicated. Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Cu²⁺, Ag⁺, AuCl₄⁻, Be²⁺, Mg²⁺, Ca²⁺, Ba²⁺, Sr²⁺, Zn²⁺, Cd²⁺, Hg²⁺, Hg²⁺, BO₂⁻, B₄O₇⁻, Al³⁺, Ga³⁺, In³⁺, La³⁺, Ce³⁺, Tl⁺, CO₃⁻, SiO₃⁻, Ti⁴⁺, Sn⁴⁺, Pb⁴⁺, Zr⁹⁺⁺, Th⁹⁺⁺, NH₄⁺, NO₂⁻, NO₃⁻, H₂PO₄⁻, P₄O₁₃⁻⁻, HPO₃⁻, P₆O₁₉⁻⁻⁻, PO₃⁻, HPO₄⁻, P₂O₇⁻⁻⁻, VO₃⁻, HAsO₃⁻, HAsO₄⁻, Sb⁴⁺⁺, Sb⁵⁺⁺, Bi⁴⁺⁺, S⁻⁻, SO₃⁻⁻, S₂O₃⁻⁻, SO₄⁻⁻, Cr⁶⁺⁺, Cr₂O₇⁻⁻, SeO₃⁻, SeO₄⁻⁻, MoO₄⁻⁻, WO₄⁻⁻, TeO₃⁻⁻, TeO₄⁻⁻, UO₄⁻⁻, UO₂²⁺, F⁻, F⁻⁻, Cl⁻, ClO₃⁻, ClO₄⁻, Mn⁷⁺⁺, MnO₄⁻, Br⁻, BrO₃⁻, I⁻, IO₃⁻, ReO₄⁻, Fe²⁺, Fe³⁺⁺, Co²⁺, Ni²⁺, RuCl₅⁻⁻, PdCl₄⁻⁻, RhCl₆⁻⁻, OsO₅⁻⁻, IrCl₆⁻⁻, PtCl₆⁻⁻, Fe(CN)₆⁻⁻⁻⁻, CN⁻, NCS⁻, acetate, oxalate, malonate, formate, adipate, succinate, phthalate, tartrate, lactate, gluconate, glycol, diethylene glycol, citrate, L-inositol, d-sorbitol, mannitol, sucrose, dextrose, aniline, pyridine.

Experimental

α-Benzoinoxime Method. A yellow precipitate is formed between α-benzoinoxime and vanadates in a strongly acidic solution. The acid greatly increases the selectivity of the test.

Reagents. α-Benzoinoxime, saturated solution in ethyl alcohol. Sulfuric acid, 3 N.

Procedure. To one drop of the oxidized solution to be tested is added two drops of the α-benzoinoxime followed by one drop of 3 N sulfuric acid.
Limit of Identification. 1 γ of V.

Limiting Concentration. 1 : 50,000.


Colored Ions Which Complicate Interpretation of Test. AuCl₄⁻, Cr⁴⁺, Fe⁴⁺, RuCl₅⁻⁻, RhCl₆⁻⁻⁻⁻, PdCl₄⁻⁻⁻⁻, IrCl₆⁻⁻⁻⁻.

ζ, ζ-Dipyridyl and Ortho Phenanthroline-Iron Method. Vanadyl ion reduces ferric iron to the ferrous state which forms a red solution with ζ, ζ-Dipyridyl and an orange solution with ortho phenanthroline in an acidic solution.

Reagents. ζ, ζ-Dipyridyl, 2% solution in 0.1 N hydrochloric acid.

Ortho phenanthroline, 2% solution in 0.1 N hydrochloric acid.

Ferric chloride, 1% aqueous solution.
Disodium phosphate, saturated aqueous solution.
Concentrated hydrochloric acid (12 N).

Procedure. One drop of the oxidized solution to be tested is placed in a micro beaker with one drop of concentrated hydrochloric acid and heated to boiling. After evaporating to half the original volume the solution is cooled and transferred to the spot plate. A drop of ferric chloride solution is added and thoroughly mixed. One drop of either reagent is added followed by a drop of the disodium phosphate solution. If the solution is too acidic prior to the addition of the reagent the color develops very slowly or possibly not at all. Normally the addition of the disodium phosphate to the acidic
solution buffers it to a pH range at which the color develops satisfactorily.

Limit of Identification. 0.1 γ of V.
Limiting Concentration. 1 : 500,000.

Interferences. Positive: I⁻, Co⁺⁺, Ni⁺⁺.
Masking: AuCl₄⁻, Cr₂O₇⁻⁻, Fe(CN)₆⁻⁻⁻, Fe(CN)₆⁻⁻⁻.

Colored Ions Which Complicate Interpretation of Test.
Cr⁺⁺⁺, RuCl₅⁻⁻, IrCl₆⁻⁻⁻.

Dimethylglyoxime-Iron Method (Improved). This test is also based on the formation of ferrous ion by vanadyl ion and the formation of a pink solution by the reaction of dimethylglyoxime with divalent iron in ammoniacal solution.

Reagents. Dimethylglyoxime, 1% ethyl alcohol solution.
Ferric chloride, 1% aqueous solution.
Disodium phosphate, saturated aqueous solution.
Concentrated ammonium hydroxide (29%).
Concentrated hydrochloric acid (12 N).

Procedure. The reduction is carried out in the same manner as described in the previous procedure. To this solution is added one drop of ferric chloride solution followed by two drops of the dimethylglyoxime reagent and one drop of disodium phosphate solution. This is thoroughly mixed and made alkaline with a drop or two of concentrated ammonium hydroxide.

Limit of Identification. 1 γ of V.
Limiting Concentration. 1 : 50,000.
Interferences. Positive: I⁻, Co²⁺, Ni²⁺.
Masking: AuCl₄⁻, Cr₂O₇⁻², IO₃⁻, PdCl₄⁻², PtCl₆⁻², Fe(CN)₆⁻⁴, Fe(CN)₆⁺².

Colored Ions Which Complicate Interpretation or Test.
Cr²⁺⁺, RuCl₅⁻, IrCl₆⁻³.

Tungstate Method. This test is based on the intensification of the colored vanadic acid in the presence of phosphoric acid by sodium tungstate. The appearance of a yellow-to-orange color indicates the presence of vanadium. Strong acids are harmful, and for this reason phosphoric or acetic acid should be used in preparing the solution.

Reagents. Phosphoric Acid, 85%.
Sodium tungstate, 10% aqueous solution.

Procedure: To one drop of the oxidised solution to be tested is added one drop of the phosphoric acid. The mixture is allowed to stand for a few seconds so that the acid can form complexes with interfering cations. A drop of 10% sodium tungstate is then added and the yellow-to-orange color develops if vanadate is present.

Limit of Identification. 0.3 g of V.
Limiting Concentration. 1 : 165,000.

Interferences. Positive: None. Masking: None.

Colored Ions Which Complicate Interpretation of Test.
AuCl₄⁻, Cr²⁺⁺, Cr₂O₇⁻², MnO₄⁻, RuCl₅⁻, RhCl₆⁻³, PdCl₄⁻², IrCl₆⁻³, PtCl₆⁻², Fe(CN)₆⁻⁴, Fe(CN)₆⁺².

Remarks
The vanadate solution used for the determination of
sensitivity was standardized by titrating the vanadium in the quadrivalent state with standard potassium permanganate solution. The reduction of the vanadate to vanadyl ion was accomplished with ferrous iron (12).

The effect of the inherent color of the ferric ion on the J -benzoinoxime test can be eliminated by complexing it with phosphate. Nickel can be prevented from reacting with dimethylglyoxime by complexation with cyanide. Oxalate masks the J -benzoinoxime test and as would be expected sucrose gives a positive test with those methods based on the reduction of ferric to ferrous iron.

The addition of the phosphate to the dimethylglyoxime improves the test by preventing the precipitation of ferric hydroxide and a number of other cations which form insoluble compounds in an ammoniacal solution. Both the J , J di-pyridyl and ortho phenanthroline react with ferrous ion in acidic solution thus eliminating the complications due to the ferric and other insoluble hydroxides. The reduction of ferric iron by vanadyl ion does not readily take place at a low pH (3). It was found however that the redox reaction will proceed satisfactorily in a solution at a pH of 6. The acidic solution on the addition of the disodium phosphate is normally buffered at pH 6-7.

Conclusion

Two spot tests for vanadium were developed. The one test involves the use of J -benzoinoxime as the reagent and the other employs J , J di-pyridyl or ortho phenanthroline.
Detailed interference studies were made on reported tests for detecting vanadium which use dimethylglyoxime and sodium tungstate as reagents. Improvements were made in the dimethylglyoxime test by adding disodium phosphate which prevents the precipitation of a number of ammoniacal insoluble ions and ferric iron which is used in the test procedure. This greatly simplifies the interpretation of the results and makes it possible to carry out the test in a spot plate.
Literature Cited

A COMPARISON STUDY OF THE COPRECIPITATION OF CATIONS BY ORGANIC AND INORGANIC PRECIPITANTS

by

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The contamination of precipitates by substances that are normally soluble under the conditions of the precipitation is an important factor in the evaluation of reagents used in gravimetric methods of analysis. The problem of coprecipitation is generally associated with the use of inorganic precipitants, but with increasing use of organic reagents in gravimetry some knowledge of the relative tendencies of organic and inorganic precipitants to coprecipitate seems highly desirable.

A general discussion of sources and types of error possible in various uses of organic reagents for inorganic analysis has been presented by West (1). In the discussion of gravimetric methods it was pointed out that a survey of accepted procedures failed to disclose information concerning coprecipitation phenomena. An exception to this statement being the work of Ryan and Painer on the gravimetric determination of palladium with 1,10-phenanthroline (2) in which is disclosed that platinum metals other than palladium fail to yield precipitates with the reagent
under test conditions: the presence of such metals during the determination of palladium, however leads to slightly high results. A study dealing specifically with coprecipitation has been made by Heck, Hunt and Mellon (3). Their study represents the first research on this type of error in the application of organic reagents to be published. This survey involved a comprehensive study of the coprecipitation phenomena of nitron nitrate and their conclusion was that only negligible error could be traced to these effects.

The apparent failure of common procedures employing organic reagents to indicate the existence of coprecipitation can be attributed to a number of possibilities. In some cases there seems to be no doubt but what the organic compounds have superior characteristics. The work of Mellon and his coworkers cited above substantiates this, and there are good theoretical grounds for believing that certain types of coprecipitation would be minimized due to complexities of bonding, spacial restrictions, and steric hinderance.

Because of the real lack of facts concerning the coprecipitation problem in the use of organic reagents, a study seemed warranted which would survey the extent of these effects. The survey was conducted on a systematic basis to establish the relative tendencies of several of the more common inorganic and organic precipitants to coprecipitate diverse cations. The precipitations with both
the organic and the inorganic reagents were carried out by accepted procedures in as similar a manner as possible and under conditions most favoring coprecipitation. The final evaluation of results was made by means of emission spectrography.

In selecting the organic reagents to be investigated care was taken to use selective reagents rather than those exhibiting wide diversity of reactions which might chemically react with extraneous ions. Reagents illustrating all types of organic-inorganic reactions of interest in gravimetry were selected. Cation precipitants functioning through the formation of chelated normal salts were illustrated by rhodazonic acid which was used to precipitate barium: comparison was made against barium sulfate. Inner-complex salt formation was studied in the use of p-dimethylamino-benzalrhodanine as a precipitant for silver; in this case comparison was made against silver chloride precipitates. A somewhat similar type of study involved the comparison of \( \alpha \)-benzoinoxime and alkali iodides as reagents for copper.

A unique type of reaction that has only been recognized recently (4) results in the formation of polynuclear complexes of large ring size. The precipitation of cupric thiocyanate and benzidine can be considered as representing this type. The final and simplest class of reaction studied was that of direct normal salt formation as shown by the thiocyanate precipitation of cuprous copper, comparison
One example of anion precipitation was studied. Normal salt formation constituted the reaction type, with actual studies being made on the precipitation of sulfate by the use of benzidine as well as by means of barium.

Experimental

Comparison studies of metallo-organic precipitates and inorganic precipitates was made by mixing equivalent amounts of precipitants and reacting metal ions. The diverse ions used to study coprecipitation tendencies were added in amounts of $2.8 \times 10^{-4}$ mole for each ion studied.

Two precipitations were made with each organic and inorganic reagent studied. One was carried out in the presence of the extraneous ions and the other in the absence of such ions, the latter shall be referred to as the pure precipitate. Both of these were prepared so that accurate spectrographic comparisons could be made by eliminating the matrix error that would have been introduced due to the different composition of the organic and inorganic precipitates under consideration. When a sample is burned in an arc or spark type discharge the composition of the matrix has a definite buffering action on the intensities of the light emitted by each element present. This difficulty was overcome by preparing the spectrographic samples in the following manner. In one case a weighed amount of the material precipitated by the organic reagent in the presence of the extraneous ions was thoroughly mixed with a weighed amount of the pure
material precipitated by the inorganic reagent that was used for comparison. The amount of the ion in each spectrographic sample was $9 \times 10^{-5}$ mole. Each of the two samples was transferred to a 5/16" cratered spectrographic electrode and exposed for two minutes under the same conditions on a photographic plate. A large Bausch and Lomb Littrow spectrograph was used with a direct current arc type excitation of 5 amperes and 200 volts.

Precipitation of Silver: Accepted procedures were followed which employed p-dimethylaminobenzalrhodamine (5) and chloride ion (6) for the precipitation of silver from silver nitrate solution. Sodium, chromium (III), manganese (II), cobalt (II), strontium, aluminum, nickel, bismuth (chloride complex), cadmium and lead nitrates were present during the precipitation.

Precipitation of Barium: Sodium rhodizonate (7) and sulfate ion (6) were the reagents used to precipitate barium from barium chloride solution. Sodium, cobalt (II), nickel, cadmium, zinc, calcium, potassium and magnesium chlorides were present during the precipitation.

Precipitation of Sulfate: Benzidine (8) and barium ion (6) were the reagents used to precipitate sulfate ion from sulfuric acid solution. Sodium, chromium (III), cobalt (II), aluminum, nickel, cadmium, zinc, calcium, potassium and magnesium were present during the precipitation.

Precipitation of copper: Thiocyanate ion plus benzidine
(9), \( \alpha \)-benzoinoxime (10), thiocyanate ion (6) and iodide ion were used to precipitate copper from cupric nitrate solution. It is recognized that copper is not normally determined gravimetrically as cuprous iodide but for the purpose of this study it is the most convenient and satisfactory. Sodium, chromium (III), aluminum, manganese (II), potassium and magnesium were present during the precipitation. Accepted procedures for precipitating copper by means of the reagents studied were followed in all cases except for that of \( \alpha \)-benzoinoxime. The reported method for precipitating copper ion with \( \alpha \)-benzoinoxime describes carrying out the reaction in an ammoniacal solution to which tartrate ion has been added in order to form soluble complexes with most of the extraneous cations that would normally precipitate in alkaline solution. In this study the precipitation was carried out at a pH below that which causes precipitation of the hydroxides of the cations present. Under this condition it was not necessary to add the tartrate. Complete precipitation of the copper was not obtained at the lower pH but this was not considered objectionable for the studies of coprecipitation.

In every case the precipitations were performed at room temperature. The reagents were added rapidly and the precipitates were immediately removed by filtration, washed and dried at room temperature.

Discussion of Results and Conclusions

The spectrograms were evaluated by visually determining
the cations which had been coprecipitated in each sample. If the same one was present in both spectrograms made from the organic and inorganic precipitate, an estimation was made as to which sample had the greater concentration.

The cations that were present during the precipitation and those which were indicated in the spectrograms as being present in the precipitates are given in Table 1. The data in Table 1 indicate that the organic precipitants in general coprecipitate cations to a greater extent than the inorganic precipitates. The favorable weight ratio of the organic reagents would tend to nullify the error introduced by the coprecipitation. This probably accounts for the fact that coprecipitation by the organic precipitates has not been observed to be significant.

It is noted that chromium was found in all of the precipitates and that aluminum was found in two. The only inorganic precipitate containing aluminum was silver chloride. Since chromium is carried down by so many different types of precipitates it is difficult to explain its presence on any other basis than physical adsorption which made it extremely difficult to wash out using distilled water containing no electrolyte. The probable mechanism in such coprecipitation involves the formation of colloidal precipitates which flocculate under the influence of electrolytes present in the immediate zone of reaction. Because trivalent ions such as chromium and aluminum would have the most favorable flocculation values
# TABLE 1

**Cations Coprecipitated**

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Cations Coprecipitated</th>
<th>Cations Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver p-dimethylamino-benzalrhodanate</td>
<td>Cr++, Al++</td>
<td>Cr++, Sr++, Na+, Cr++, Mn++</td>
</tr>
<tr>
<td>Silver chloride</td>
<td>Cr++, Al++</td>
<td>Al++, Ni++, Bi++, Cd++, Pb++</td>
</tr>
<tr>
<td>Barium rhodizonate</td>
<td>K+, Na+, Cd++</td>
<td>Na+, Co++, Ni++</td>
</tr>
<tr>
<td>Barium Sulfate</td>
<td>K+ (trace), Na+</td>
<td>Zn++, Ca++, K+, Mg++, Cd++</td>
</tr>
<tr>
<td>Benzidine sulfate</td>
<td>K+, Na+, Cr+++</td>
<td>Na+, Cr+++, Co++</td>
</tr>
<tr>
<td></td>
<td>Al+++</td>
<td>Al++, Ni++, Cd++</td>
</tr>
<tr>
<td>Barium sulfate</td>
<td>K+ (trace), Na+</td>
<td>Zn++, Ca++, K+, Mg++</td>
</tr>
<tr>
<td>Cupric thiocyanate benzidine</td>
<td>Cr++, Al+++</td>
<td></td>
</tr>
<tr>
<td>Cuprous iodide</td>
<td>Cr+++ (trace)</td>
<td>Na+, Cr+++, Al+++</td>
</tr>
<tr>
<td>Cuprous thiocyanate</td>
<td>Cr+++ (trace)</td>
<td>Mn++, K+, Mg++</td>
</tr>
<tr>
<td>Cuprous iodide</td>
<td>Cr+++ (trace)</td>
<td></td>
</tr>
<tr>
<td>Cupric benzoinoxime</td>
<td>Cr+++</td>
<td></td>
</tr>
<tr>
<td>Cuprous iodide</td>
<td>Cr+++ (trace)</td>
<td></td>
</tr>
</tbody>
</table>
they would be closely associated with the flocculation and as a consequence would be most liable to be carried down with the precipitate.

It should be pointed out again that this experimental work was carried out under conditions most favoring coprecipitation. In actual practice much of the coprecipitation can be avoided or eliminated by employing such standard technics as precipitating slowly at an elevated temperature, digestion and washing with solutions of volatile electrolytes. The use of volatile electrolytes would be particularly valuable in the elimination of coprecipitated ions adsorbed on the surfaces during flocculation.
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SUMMARY

1. A spot test for detecting antimony which uses gossypol as the reagent has been developed. Considering all of the requirements for a good spot test, gossypol appears to be superior to any other reagent for antimony which has been previously reported in the literature. It is sensitive, highly selective, stable and readily available. The spot test procedure is very simple, requiring no elaborate conditioning treatments or specialized technics.

2. A spot test for vanadium has been developed which uses \( \alpha \)-benzoinoxime as the reagent. This is a sensitive and highly selective test and is less affected by colored ions.

3. A spot test for vanadium using \( \alpha, \alpha \)-dipyridyl or ortho phenanthroline with iron has been developed. This is more sensitive than any test reported previously in the literature and is highly selective.

4. Detailed interference studies have been made on the use of dimethylglyoxime and iron in the spot test detection of vanadium. The reported procedure has been improved by simplifying the interpretation of the test results.

5. Detailed interference studies have been made on the use of sodium tungstate for the detection of vanadium. This method has no chemical interferences but the presence of colored ions make interpretation of the test difficult.
A study has been made of the relative tendencies of organic and inorganic precipitants to coprecipitate extraneous cations. Six comparisons were made and the data indicate that the organic precipitates tend to coprecipitate cations to a greater extent than inorganic precipitates. Some speculation has been offered to explain this. The final evaluation of this work was done by emission spectrography.
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VITA

Louis Johnson Conrad was born in Harrisburg, Pennsylvania, on September 28, 1917 and received his elementary and secondary education in the public schools there.

In June, 1939 he received the degree of Bachelor of Science from Lebanon Valley College at Annville, Pennsylvania. In June, 1941 he was granted the degree of Master of Arts in Chemistry from the University of North Carolina, Chapel Hill, North Carolina.

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EXAMINATION AND THESIS REPORT

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Major Field: Chemistry

Title of Thesis: Selected Studies of Organic Reagents

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: May 11, 1950