

MICROCHEMISTRY OF THE PRECIOUS METAL ELEMENTS

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INTRODUCTION

The precious metal elements to be discussed in this paper are platinum, palladium, rhodium, ruthenium, iridium, osmium and gold. Considerable attention has been devoted successfully in the past to means of identifying gold and silver in minerals, but the microchemistry of the remaining six elements has been generally neglected. In part, this neglect results from the complex chemical behavior of these elements and, in part, from the assumption that the platinum-palladium group of minerals are rare. Recent discoveries of noteworthy amounts of several of these elements in many ores emphasize the need of some method whereby the composition of unknown minerals encountered during mineragraphic investigations can be tested for the presence of the precious metal elements.

The need for distinctive microchemical tests is increased because all of these seven elements are known to form natural alloys with one or more of the others, and isomorphism among the proved minerals is known for some of these elements and suspected for others.

The elements mentioned above can be divided into two groups on the basis of their atomic weights and chemical behavior. The silver group—consisting of silver, palladium, rhodium and ruthenium—have atomic weights ranging from 107.8 to 101.7. The gold group contains the heavier elements (gold, platinum, iridium and osmium) with atomic weights between 195.7 and 191.0. Each group shows many chemical similarities but in general it is much more difficult to distinguish between individual members of the two groups than between members of separate groups. Considerable difficulty has been encountered in distinguishing platinum from iridium, or palladium from rhodium. Silver is omitted from the interference studies and discussions because, unlike the other seven elements, it does not form a soluble chloride.

The ideal test would, of course, be one that is distinctive, sensitive and specific for a given element under all conditions and in the presence of any or all of the other elements. Such a test is difficult to obtain, particularly for elements as closely related chemically as those under consideration. In the following discussion, particular attention is given to those tests which are distinctive for one element in the presence of the other elements, and also to the modifying or interfering effect of each of the elements on any test.

Discussion of interferences is confined to the seven elements studied. While it is well known that other elements may occur in the same mineral as several of the elements studied, none of the precious elements, except palladium, is soluble in dilute nitric or dilute hydrochloric acid. Consequently the other base elements, which are soluble in one or other of these acids, can be leached from the decomposed mineral before the precious elements are taken into solution. When palladium is present, a preliminary leaching with *dilute* hydrochloric acid will remove or fix in insoluble form any elements which are likely to be associated with palladium and which might interfere with the dimethylglyoxime test for palladium.

In the course of this study the behavior of many reagents with these elements has been investigated, but only those which give a reliable and distinctive test with one or more of the elements are mentioned in this paper. The reactions between many of these reagents and individual elements have been mentioned or discussed in numerous places in the chemical literature. The author has drawn freely on Chamot and Mason,¹ Behrens and Kley,² Wagner,³ Mellor,⁴ Watson,⁵ and the Abstracts of the American Chemical Society. Many of the previously recommended tests, although entirely satisfactory for a single element, were found to be useless in the presence of any interfering element, either because the test failed to work or because the product was so changed in color, form, or appearance as to be unrecognizable. Consequently, the reagents have been chosen, not only because they give a test with a particular element, but also because that test is distinctive under the microscope and is not seriously affected by the presence of other elements.

MINERALOGY OF THE PRECIOUS METAL ELEMENTS

The following brief summary of the mineralogical occurrences of the precious metal elements is not exhaustive but presents most of the established natural alloys and minerals so that the worker may have a knowledge of the possible combinations of elements and the likely interfering elements encountered in testing for the precious elements.

PLATINUM

Platinum occurs as the native metal, rarely pure, commonly alloyed

¹ Chamot, E. M., and Mason, C. W., *Handbook of chemical microscopy*, New York, 1931.

² Behrens-Kley, *Mikrochemische Analyse*, Voss, Leipzig, 1921.

³ Wagner, P. A., *Platinum deposits and mines of South Africa*, London, 1929.

⁴ Mellor, J. W., *A comprehensive treatise of inorganic and theoretical chemistry*, vol. XV, Longmans, Green and Co., New York, 1936.

⁵ Watson, J. A., Colour reactions in the micro-chemical determination of minerals: *Mineral. Mag.*, vol. 24, No. 148, pp. 21-34, March 1935.

with iron, copper, gold, or other members of the precious metal group. The following tabulation gives many of the native platinum alloys.

TABLE 1*

	Pt	Pd	Rh	Ru	Ir	Os	Au	Fe	Cu
Platinum	100								
<i>a</i> -Ferroplatinum	71-78	0.2-0.8			1-4.5			16-21	
<i>b</i> -Ferroplatinum	73-78							16-20	
<i>a</i> -Polyxene	80-90	0-2.5			1-5.5			6-11	
<i>b</i> -Polyxene	80-90							6-10	
Cuproplatinum	70	0-0.25			1-2			12-15	8-13
Platiniridium	56				4			28	
Iridium	20				77				
Palladic platinum	73-84	3-22			0-3.6				
Rhodic platinum			4.6						
Platinic iridosmium	10.1		1.5		55.2	27.3			
Iridic gold	3.8				30.4		62.1		
Platinic iron	8.2							91.8	

* This table and the following discussion is based mainly on data given in Wagner, *op. cit.*, pp. 11-12, and Mellor, *op. cit.*, pp. 498, 545, 592-93, 686, 730.

Sperrylite (PtAs_2) is the most abundant of the platinum minerals, although Cooperite (PtS) and Braggite (Pt, Pd, NiS) are also found in small amounts.

The solubility of the platinum alloys varies greatly depending on the composition of the alloy. Those containing substantial amounts of iron or copper are fairly readily soluble in aqua regia. Those containing much osmium or iridium are not soluble in aqua regia. The arsenide and sulphide platinum minerals are slightly soluble in aqua regia but the rate of decomposition is very slow. Some sperrylite appears to be untouched by aqua regia. Cooperite is insoluble in aqua regia.

PALLADIUM

Palladium occurs as the native metal but like platinum it is commonly alloyed with other elements. In addition to the palladium-bearing alloys mentioned in Table 1, palladic gold containing 8 to 11.6 per cent palladium, 86 to 91 per cent gold, with small amounts of silver, and potarite—an alloy of palladium and mercury, are also found as minerals.

Stibiopalladinite, Pd_3Sb , is the only known palladium antimonide. Braggite (Pt, Pd, NiS), carries up to 20 per cent palladium. Allopladium has been reported to contain palladium, silver, gold and selenium. Also, clausenthalite is reported to contain mercury and palladium, plumbojarosite up to 0.2 per cent, and covellite may carry some palladium.

Whether the palladium in these last three minerals is present as inclusions or as solid solution is not certain.

Palladium differs from the rest of the precious element group in that several of the palladium minerals are readily decomposed by nitric acid. Palladium, particularly if alloyed with gold or silver, dissolves in dilute nitric acid. Fine grained palladium is soluble in concentrated nitric acid, concentrated hydrochloric acid or aqua regia.

RHODIUM

Little is known concerning the mineralogy of rhodium. In addition to the alloys mentioned in Table 1, rhodite contains 34 to 43 per cent rhodium together with gold and some silver, and rhodium-bearing osmiridium and iridosmium contain up to 17.2 per cent. Most platinum minerals carry some rhodium, in rare specimens the rhodium content reaches 5 per cent. Sperrylite may contain up to 0.72 per cent rhodium.

Metallic rhodium is not soluble in aqua regia unless alloyed with gold, copper, lead, bismuth or platinum.

RUTHENIUM

Ruthenium is present in osmiridium up to 8.5 per cent, in ruthenic osmiridium up to 18.3 per cent, and in ruthenic iridosmium up to 13.4 per cent. The ruthenium sulphide, laurite (RuS_2) or $(\text{RuOs})\text{S}_2$ is also known.

Ruthenium is reported to be soluble in concentrated HCl but laurite is only slightly attacked by aqua regia.

IRIDIUM

The commonest occurrence of iridium is alloyed with osmium to form the natural alloys osmiridium, containing up to 17 per cent iridium, and iridosmium with 47 to 77 per cent iridium. Osmite contains 10 per cent iridium and many of the platinum minerals also carry iridium (Table 1). Iridic gold carries up to 30.4 per cent iridium. No sulphides or arsenides of iridium are known. Most iridium compounds are insoluble in aqua regia.

OSMIUM

All of the important osmium alloys have been already mentioned. No sulphide or arsenide of osmium is known, although laurite may contain up to 3 per cent osmium. Osmium alloys in general are not soluble in aqua regia.

GOLD

Gold occurs in natural alloys with some of the precious metal group to form minerals such as palladic gold (sometimes called porpexite) containing 86 to 91 per cent gold, rhodite (rhodic gold), iridic gold and platinic gold. The ordinary gold minerals are well known. Although most of the gold alloys and minerals are decomposed by nitric acid, the gold is soluble only in aqua regia.

SOLUTION OF SAMPLE

From the preceding discussion it is evident that the precious metal elements and minerals differ greatly in their solubility. Some are soluble in nitric acid, some in aqua regia, and some are practically insoluble in any ordinary acid. The presence of osmium or iridium in a mineral or alloy usually increases its insolubility. All of these eight elements, except silver however, are soluble as chlorides and can be converted into that form by means of the well known method of fusion with sodium chloride in a chlorine atmosphere. This method is best suited to larger quantities of material than are used in ordinary microchemical tests, but by skillful manipulation it is possible to apply the method to very small samples.

For the present investigation, a pure sample of gold chloride was dissolved in distilled water to make a solution containing 1 per cent of the element by weight. Samples of chemically pure platinum, palladium, rhodium, ruthenium, iridium and osmium were treated as follows.

A weighted quantity of the element was ground in an agate mortar with about four times its weight of fused sodium chloride and the mixture placed in a small, hard, open, glass tube. The tube was then connected with a chlorine generator and carefully heated until the mass gently glowed. This treatment was continued for three minutes, then the tube was disconnected and its contents allowed to cool. The contents of the tube were dissolved in distilled water and filtered. Any undissolved residue was again treated in a similar manner. Ordinarily two fusions are sufficient. The resulting solution was then made up to such volume as to contain 1 per cent of the metal by weight. Any silver present is, of course, converted into the chloride, insoluble in acids or water but soluble in ammonium hydroxide.

Avoidance of overheating is necessary, particularly with platinum, the chloride of which is readily decomposed by excess heat. With care, however, all of the elements can be obtained as soluble chlorides by this method which has also been recommended for use in quantitative analysis.⁶ The colors of the solutions may be of some assistance in de-

⁶ U. S. Bureau of Standards Notes. *Jour. Franklin Institute*, vol. 217, Jan. 1934, pp. 106-107.

termining the dominant elements present. Thus the 1 per cent solution of gold is yellow; platinum and osmium, yellow with a faint tinge of orange; iridium, brown; palladium, brownish red; rhodium, cherry red; and of ruthenium, dark cherry red.

PROCEDURE

The elements studied are thus present as compound chlorides of the element and sodium, except gold, which is in solution as gold chloride. The solution of each element in distilled water contains either 1 per cent or 0.1 per cent of the element by weight.

The reagents are used in the strengths indicated in the following section. Potassium iodide and ammonium chloride are used in the solid form. When using potassium iodide, only a small fragment is added to the test drop; with ammonium chloride sufficient quantities are added to give a slight excess of the reagent.

The reactions between individual elements and the reagents are mostly run on a 1 per cent solution of the element. If the element gives a useful reaction, the test is repeated on a 0.1 solution. In the study of interferences, tests are first made using a drop of a 0.1 per cent solution of the element to be tested added to a drop of a 1 per cent solution of the other, possibly interfering, element. If no interference is obtained the test is considered satisfactory. If there is interference, the test is repeated using a 1 per cent solution of each element. If no test is then obtained, the test is considered useless. If, however, this test is free from interference, it is recorded but appears in a different column in Table 2.

The rate of formation of the precipitate is noted in the description of each test. In part this is determined by the concentration of the solution but since all or nearly all of these elements react with many of the reagents, the relative solubility of the precipitates frequently affords a useful distinction. Consequently the relative rapidity of precipitation is a valuable criterion. Accordingly all tests are observed and successive reactions noted until the drop evaporates. While only those tests which give rapid precipitation are recommended, it frequently happens that much additional information concerning other elements in solution can be obtained by observing the test drop until it is dry.

For each reagent studied, the reaction of the individual elements is first presented and is followed by interference reactions for those elements which give a useful precipitate with the reagent.

The following abbreviations and symbols are used throughout the description of tests.

- D. L. Transmitted light. When the color of a precipitate is given without designation, it is to be assumed that the observation was made in transmitted light.

R. L. Reflected light.

(1) A solution containing 1 per cent by weight of the element.

(0.1) A solution containing one tenth per cent by weight of the element.

REAGENTS AND THEIR STRENGTHS

Benzidine	0.05 gm. benzidine dissolved in 10 cc. glacial acetic acid, dilute to 100 cc. with distilled water.
Thiourea	10 per cent solution in water.
Dimethylglyoxime	1 volume of 2 per cent solution in alcohol added to 1 volume of water.
Dimethyl-amino-benzal-rhodanine	0.03 per cent solution in acetone.
Pyridine-hydrobromic acid	1 volume of pyridine added to 9 volumes of 40 per cent HBr. Solution deteriorates rather quickly.
Potassium mercuric thiocyanate	5 per cent solution in water.
Ammonium bichromate	A solution in water of such strength as to give a good silver test with a one tenth per cent solution of silver, i.e., approximately 0.1 gm. of the salt in 30 cc. of water.
Potassium bichromate	A solution of the same color intensity as that for ammonium bichromate.
Potassium iodide	Solid
Ammonium chloride	Solid
Cesium chloride	Solid

DETAILED INVESTIGATION OF TESTS

AMMONIUM BICHROMATE

Individual Reactions

1 per cent solution	
Platinum	Immediate precipitation of feathery crosses, cubes and octahedrons. Dark in D.L., yellow in R.L.
Palladium	Bichromate slowly produces a strong precipitation of feathery crosses and jagged three pointed stars, brown to black in D.L., reddish brown in R.L. Slow but strong test.
Rhodium	No precipitate until drop evaporates.
Ruthenium	Bichromate produces a fairly rapid precipitation of very small red grains, red in R.L.
Iridium	Immediate precipitation of black cubes, cube-octahedron forms, rhombs and crosses, black in R.L. Forms are larger and better developed than with potassium bichromate.
Osmium	Immediate precipitation of orange-to-black rhombs and hexagons.
Gold	No precipitate.

Interference Tests

Pt (1) Ir (1)	Immediate precipitate of orange to black crystals, wine-red in R.L. First crystals precipitated are iridium, then mixed crystals, and finally yellow platinum forms. Strong test.
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AMMONIUM CHLORIDE

Individual Reactions

1 per cent solution	
Platinum	Immediate copious precipitate of feathery crosses, cubes, feathery three, four, and five pointed stars; dark in D.L., very faint yellow in R.L.

Palladium	Slow formation of long yellow needles which in some tests grow across drop. Needles are pleochroic, from golden yellow to grass green; straight extinction, high birefringence.
Rhodium	No precipitate until drop is partly evaporated. Then tiny dark cubes with a high index first form, followed by large pink hexagons and petals. These are usually thin and have a moderate index. Test is very characteristic but slow in forming.
Ruthenium	No precipitate until drop is partly evaporated. Then slowly tiny yellow cubes form and become dark as they grow. Excess reagent becomes stained dark yellow. Later, a few crosses may form and sometimes, just as drop dries, pinkish brown hexagons may appear. Test is not distinctive or reliable.
Iridium	Immediate precipitate of tiny black cubes around reagent. Cubes very small but very abundant. Black in R.L.
Osmium	Immediate and copious precipitation of medium-sized, reddish brown to black cubes, three and four pointed stars, and octahedrons. Reddish brown in R.L.
Gold	No precipitate even in dry drop. Ammonium chloride blades are colored yellow in dry drop.

Interference Tests

Pd (0.1)	Yellow palladium spines form just before drop dries, weak test.
Pd (0.1) Rh (1)	Pink rhodium hexagons slowly form on edge of drop, strong rhodium test, no trace of palladium.
Pd (1) Rh (0.1)	Fairly quick development of good yellow palladium spines. No rhodium test.
Os (0.1) Ru (1)	Add NH_4Cl in excess, rapid precipitation of reddish brown to black cubes and octahedrons; reddish brown in R.L., copious precipitate of osmium. No interference from ruthenium.

BENZIDINE

Individual Reactions

1 per cent solution	
Platinum	Quick formation of long, thin, hairlike needles, green to yellow green, straight extinction, high birefringence in thicker needles; yellowish white in R.L. Needles usually single units, but sometimes several will radiate from a common center. Very distinctive form and test.
Palladium	No immediate precipitate. As drop evaporates, radiating needles and branching blades grow from the edge, showing brownish yellow in D.L., yellow in R.L. Test is slow to start but strong before drop dries.
Rhodium	No immediate precipitate. Slow formation of spherules and rounded grains; pink to yellowish black in D.L., rose pink in R.L. Slow but strong test.
Ruthenium	No immediate precipitation. As drop dries, rounded grains and spherules, or a few needles (sometimes both), all faintly yellowish in D.L., yellowish orange in R.L. form. Slow test, but strong. Forms not very distinctive.
Iridium	Immediate precipitation of small, faint yellow to black, isometric grains with a high index of refraction; light yellow in R.L. Strong test.
Osmium	After about 15 seconds, long, brilliant yellow blades form. Straight extinction, faintly pleochroic, from light to dark yellow. Yellow in R.L.
Gold	Slow formation of yellow needles and clusters around edge of drop. Strong test as drop dries.

Interference Tests

Platinum

- Pt (0.1) Pd (1) Long yellow needles and blades form slowly from edge of drop, later developing into branching blades and typical palladium forms. Platinum test is distinct.
- Pt (1) Pd (1) Immediate precipitation of hair-like needles, followed much later by palladium blades. Strong platinum test.
- Pt (0.1) Rh (1) Yellow needles first grow from edge of drop (typical platinum form), somewhat later there is precipitation of faint pink, rounded grains, high index of refraction. Faint pink also in R.L. Both elements show up clearly.
- Pt (0.1) Ru (1) Yellow platinum needles quickly form from edge of drop. As drop evaporates, rounded grains, faint yellow in D.L., brownish-pink in R.L. slowly form. Ruthenium forms appear in abundance just before drop dries. Satisfactory test for both elements.
- Pt (0.1) Ir (1) Immediate precipitation of small, round-to-irregular shaped grains; very high index; dark in D.L., faint yellow in R.L. Later a few yellowish green blades may form. Strong test, but platinum needles and blades may not appear.
- Pt (1) Ir (1) Same precipitate as above. Platinum needles may or may not appear.
- Pt (0.1) Cs (1) Immediate precipitation of yellowish green needles which appear more abundantly and more quickly than from platinum solution alone. No trace of osmium blades.
- Pt (0.1) Au (1) Yellow-to-purple clusters of very small needles and small grains slowly form. Later typical platinum needles grow from edge of drop.

Osmium

- Os (0.1) Rh (1) Quickly forms good rhodium spherules, dark to yellow in D.L., faint pink in R.L. No trace of osmium forms.
- Os (1) Rh (1) Rhodium spherules quickly form, then large yellow osmium blades. Good test for both elements.
- Os (0.1) Pd (1) Slowly, yellowish brown acicular clusters of roughly round shape appear. These are the palladium precipitate, no trace of osmium.
- Os (1) Pd (1) Strong rapid growth of yellow osmium blades, as drop evaporates yellow-brown palladium clusters slowly appear.

Rhodium

- Rh (0.1) Pd (1) A few rhodium spherules are formed, but not until after most of the palladium has precipitated. Test not satisfactory for rhodium.
- Rh (1) Pd (1) Immediate precipitation of rhodium spherules. Strong test. After drop is partly evaporated, greenish-yellow palladium clusters form and partly mask rhodium spherules. Definite test for both elements.
- Rh (1) Pd (0.1) Immediate precipitation of abundant rhodium spherules. Practically no trace of palladium even as drop dries. Since a tenth per cent solution of either rhodium or palladium alone gives a good test, it appears that the element predominating in a test drop determines the form of the precipitate.

CESIUM CHLORIDE

Individual Reactions

1 per cent
solution

- Platinum Immediate precipitation of long, greenish brown needles radiating out from

grain of CsCl. Needles have many branching arms at right angles. Later feathery crosses, poorly shaped cubes and irregular grains form. All are golden brown in R.L. Isotropic.

Palladium	Immediate fine-grained precipitate, black in D.L., yellowish brown in R.L. Isotropic.
Rhodium	Immediate fine-grained precipitate, yellowish brown in D.L., pinkish in R.L. Beyond the ring of fine-grained precipitate, good needles and acicular clumps form. Some of needles are birefringent with parallel extinction.
Ruthenium	Immediate fine-grained precipitate, brownish golden in D.L., same color in R.L.
Iridium	Immediate fine-grained precipitate, brown to black in D.L., pinkish brown in R.L. Later, good hexagons and stars slowly form.
Osmium	Immediate fine-grained precipitate, lemon yellow in center of drop, dark to black on outer edge of precipitate. Feathery crosses and branching forms slowly develop. All lemon yellow in R.L.
Gold	Immediate precipitate of a fine-grained aggregate, greenish yellow to reddish in R.L. Followed by growth of cubes, three and four pointed stars, and octahedrons, dark to yellow brown in D.L., whitish to yellow in R.L. Then slow growth of cube-octahedron crystals, yellow in D.L., dark in R.L., and straw yellow petals and platy forms. All have a high birefringence.

DIMETHYL-AMINO-BENZAL-RHODANINE

Individual Reactions

1 per cent solution	
Platinum	No precipitate.
Palladium	Strong pink color in solution. Immediate precipitation of pink needles and clusters. Presence of 1:5 HCl prevents coloration of solution but not formation of precipitate. Color shows up best in a (0.1) solution.
Rhodium	Color of solution gradually changes from normal faint pink to yellow, with precipitation of tiny pink needles. Reaction best seen in a (0.1) solution.
Ruthenium	Immediate precipitation of colorless to yellowish brown needles, and radiating clusters. Low birefringence. Yellowish in R.L.
Iridium	No definite precipitate.
Osmium	No definite precipitate.
Gold	Immediate precipitation of a purplish fine-grained aggregate, which slowly changes in color to yellow green; then a mass of small yellow green needles form, white in R.L. Still later red hairy clusters, red in R.L. may also appear. Strong test.

Interference Tests

Ruthenium	
Ru (0.1) Pt (1)	Rather slow precipitation of ruthenium needles, some clusters, but most as single units, colorless, faint yellow or faint blue green. Straight extinction, low birefringence. Good test but it forms slowly.
Ru (0.1) Pd (1)	Copious precipitate of fine-grained needles and strong pink color in solution.
Ru (0.1) Rh (1)	Immediate development of a strong pink color in solution followed by precipitation of fine-grained needles, colored pink. Color of solution gradually fades.

- Ru (0.1) Ir (1) Immediate precipitation of needles and clusters of ruthenium. No sign of iridium.
- Ru (0.1) Os (1) Immediate precipitation of ruthenium needles and clusters. No trace of osmium.
- Ru (0.1) Au (1) Immediate precipitation of purple fine-grained aggregate, color gradually turns green and green needles appear. No trace of ruthenium test.
- Ru (1) Au (1) Immediate precipitation of purple to green precipitate, also ruthenium clusters and needles quickly appear. Good test for both elements.

DIMETHYLGLYOXIME

Individual Reactions

- 1 per cent solution
- Platinum No precipitate. Drop dries to colorless blades and prisms with blue and yellow interference colors.
- Palladium Immediate heavy precipitation of felted needles, yellow in D.L., pale green with a tinge of yellow in R.L. After standing, the precipitate recrystallizes into larger needles which are darker and greener in D.L., almost colorless in R.L. Dried drop is pinkish.
- Rhodium Precipitation in a few seconds of a very fine-grained mass of small needles, sometimes felted, dark in D.L., greenish yellow in R.L. As drop dries, faintly pink blades and feathery crosses form; needles become greenish. Test very similar to that for palladium except that needles lack yellow color in D.L. Dry drop is pink.
- Ruthenium No precipitate. As drop dries, dark feathery blades form, with black cubes also deposited just before drop is dry. Dry drop is pink.
- Iridium No precipitate. As drop dries, dark blades and stumpy forms are precipitated. Dry drop is colorless.
- Osmium Slowly precipitates yellowish blades and stumpy forms. Dry drop is yellowish.
- Gold Slow precipitation of an aggregate of small needles and stumpy prisms, colorless to faint greenish in D.L., practically colorless in R.L. Needles rarely branch but in general, precipitate cannot be readily distinguished from that of palladium or rhodium if they are present.

Interference Tests

- Pd (0.1) Pt (1) Immediate precipitate of palladium forms. Add benzidine and get good platinum test.
- Pd (0.1) Rh (1) Immediate precipitate but cannot tell whether it is palladium or rhodium. Much of precipitate dissolves in conc. HCl.
- Pd (0.1) Ru (1) Immediate precipitate of palladium forms. Add rhodamine and just before drop dries get a fair Ru test. Drop dries brown.
- Pd (0.1) Ir (1) Immediate precipitate of palladium forms. Add ammonium bichromate. Typical iridium forms appear, but palladium forms slowly disappear and palladium reprecipitates as the chromate.
- Pd (0.1) Os (1) Immediate precipitate of palladium forms. No trace of osmium.
- Pd (0.1) Au (1) Immediate precipitation but cannot tell whether of palladium or gold. Much of precipitate dissolves in conc. HCl.
- Pd (0.1) Conc. HCl Immediate precipitate of palladium forms.

Rh (1) Conc. HCl	No precipitation. Rapid precipitation, however, in presence of 1:5 HCl.
Au (1) Conc. HCl	No precipitation. Rapid precipitation, however, in presence of 1:5 HCl. Palladium can be distinguished from rhodium and gold with dimethylglyoxime by strongly acidifying the test drop with conc. HCl. The addition of 1:5 HCl will not prevent the precipitation of rhodium or gold glyoximes. The rhodium precipitate is readily soluble in conc. HCl; the gold precipitate is slowly soluble and requires a considerable excess of conc. HCl in the test drop.
Pd (0.1) Rh (1) conc. HCl	Immediate precipitation of palladium in about the same quantity as from a drop of (0.1) Pd without acid.
Rh (1) Pd (1)	Add conc. HCl and dimethylglyoxime, good palladium test no rhodium test, filter, and try A or B; A—Add benzidine; slowly get strong test of poorly formed dark spherules and irregular grains, faint pinkish tinge in reflected light. Very strong test but slow. B—Add KI; solution turns reddish brown, immediate precipitation of dark fine-grained aggregate that spreads as a ring from reagent, partly soluble in excess KI. Yellow in reflected light. Forms not distinctive but strong test. C—Add $K_2Hg(CNS)_4$, no precipitate until dry.
Ru (1) Pd (1)	Add conc. HCl and dimethylglyoxime. Good palladium test, filter, A—Add thiourea and heat; strong greenish blue color. B—Add rhodamine; copious precipitate of yellow needles and cubes.
Os (1) Pd (1)	Add conc. HCl and dimethylglyoxime, good palladium test, filter, A—Add thiourea; strong pink color for osmium.

POTASSIUM BICHROMATE

Individual Reactions

1 per cent solution

Platinum	Immediate precipitation of yellow cubes, rhombs, and other forms, light yellow color in R.L.
Palladium	Rapid growth of long, colorless to light yellow needles, high birefringence, followed by brown feathery crosses and grains, red in R.L.
Rhodium	Rapid formation of blades (as in palladium test) which seem to break down to give a fine-grained precipitate. As drop evaporates, pink ragged blades form at edge of drop. Sometimes no precipitate is formed.
Ruthenium	Immediate development of a yellowish brown color in test drop. No precipitate until drop is nearly dry, then blades and needles form around edge of drop. No distinctive test.
Iridium	Immediate precipitation of black cubes, rhombs, three pronged stars and cube-octahedron forms. Color black in both D.L. and R.L.
Osmium	With excess of bichromate, precipitation of forms is similar to iridium but red in both D.L. and R.L. Good test but requires either excess of reagent or time for concentration by evaporation.

Gold As drop dries a few spines, slightly darker yellow than bichromate grow in drying drop.

Interference Tests

Ammonium bichromate or

Potassium bichromate 1 per cent solutions of either palladium or rhodium give precipitates with the solid reagent that cannot be distinguished by form or color.

POTASSIUM IODIDE

Individual Reactions

1 per cent solution

Platinum Immediate change in color of solution to rich brown followed by rapid precipitation of small black grains which grow to hexagons and rhombs with accompanying bleaching of solution to pinkish or colorless. All crystals are black in R.L.

Palladium Instantaneous precipitation of dense, very fine-grained, chocolate brown to black powder which spreads as a ring from the KI. Color of powder is black to golden brown in R.L.

Rhodium Rapid precipitation of needles, radiating clusters, blades and stumpy prisms, solution turns yellow. All forms are highly birefringent, pink in D.L., pink in R.L.

Ruthenium No precipitation until drop dries, then small yellowish needles form at edge, golden yellow in R.L. Drop dries brown.

Iridium No precipitate. As drop dries, colorless hexagons grow and slowly stain yellow. Drop dries colorless.

Osmium Rapid precipitation of small, reddish brown to black cubes and octahedra. As drop dries, brownish blades, crosses and triangular grains grow at edge of drop.

Gold Drop immediately develops a rich brown to golden yellow color followed by immediate precipitation of a dark fine-grained aggregate yellow to brown in R.L. Later, greenish yellow cubes, petals and other forms develop in brown solution. All of precipitate is a mixture of yellow and brown under crossed nicols. Copious precipitate.

Interference Tests

Pt (1) Ir (1) Add KI. Strong platinum test. Filter,
A—Add ammonium bichromate, good iridium test of red hexagons and black cubes.
B—Add benzidine, good yellow spherules, no platinum test.

Os (1) Ir (1) Add KI. Strong osmium test. Filter,
A—Add benzidine, slowly get good iridium test of yellow octahedrons and spherules. Strong test.
B—Add ammonium bichromate, weak test and hard to tell iridium forms from osmium-iodide precipitate.
C—Add thiourea, exceedingly faint osmium test, practically negative, showing that practically all of osmium was precipitated by the KI.

POTASSIUM MERCURIC THIOCYANATE

*Individual Reactions*1 per cent
solution

Platinum	Rapid precipitation of lemon-yellow octahedra and crystals showing cubic and octahedral faces, also some feathery crosses. Isotropic. Color—greenish yellow in thin crystals to black in thick. All colored canary yellow in reflected light.
Palladium	Immediate color change from yellow to yellowish-brown color at junction of drops, followed by precipitation of chocolate brown, rather acicular crystals. Greenish yellow to orange in R.L. As drop dries, pale greenish yellow radiating branches grow.
Rhodium	Immediate precipitation of tiny black grains, white in R.L. As solution dries, branching spines develop with a pale pink color and strong birefringence.
Ruthenium	Slow precipitation of tiny black grains, white in R.L. Test drop turns yellow. Small dark crosses, reddish brown in R.L., form at edge as drop dries.
Iridium	A few small black grains appear but no characteristic precipitate. As drop dries, small pale yellow rectangular needles and crosses form at edge.
Osmium	First forms a few small black cubes, yellowish in R.L. Then slowly at edge of drop, cubes, feathery crosses, dendrites and blades appear, ranging in color from yellow in thin blades to reddish or dark brown in thick crystals. Reddish brown in R.L. No birefringence.
Gold	Immediate copious precipitate of clusters of branching needles, brownish green to brown in direct light, faint yellowish white to reddish in reflected light. Form of precipitate similar to that for copper. Very strong test.

Interference Tests

Pt (1) Ir (1)	Add $K_2Hg(CNS)_4$ —Good platinum test, filter and then add A—Benzidine; strong iridium test of yellow spherules, no Pt test. B—Ammonium bichromate; fair iridium test, no platinum test. Potassium mercuric thiocyanate plus ammonium bichromate— no precipitate.
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PYRIDINE

*Individual Reactions*1 per cent
solution

Platinum	No immediate precipitate. As drop dries, yellow prisms, rhombs, and cubes gradually form. Color at first is bright yellow but this gradually deepens to reddish yellow. Pleochroism faint yellow to yellow, moderate index, straight extinction, yellow to reddish yellow in reflected light. Slow but strong test that forms before drop is dry. Insoluble in excess reagent.
Palladium	No immediate precipitate. Very slowly, as drop evaporates, from edge of drop brown rhombs and petals grow into drop. Pleochroic from colorless to brown, straight extinction, abnormal blue interference colors. Strong test but very slow, which forms before drop is dry. Red in reflected light. Forms insoluble in excess reagent.
Rhodium	No immediate precipitate. A few faintly pinkish irregular grains and prisms form just before drop dries. Test practically negative. Forms soluble in excess reagent.

Ruthenium	No immediate precipitate. Slowly as drop evaporates, green cubes, petals and prisms, all very thin, and brown grains and prisms form in drop. Green crystals show deep blue interference colors, blue in reflected light. Red grains are red in reflected light. Strong test but slow; develops in drop before it dries. Insoluble in excess reagent.
Iridium	No immediate precipitate. In drying drop, a few yellow crosses and faintly green cubes form just before drop dries. These are soluble in excess reagent. Test practically negative.
Osmium	No immediate precipitate. As drop evaporates, yellow cubes and petals form around margin. Moderately strong, distinct test. Practically insoluble in excess reagent.
Gold	Immediate copious precipitate of clusters, prisms, needles and feathery forms. Pleochroic from pale yellow to blood red, low extinction, red in reflected light. Strong, distinctive test.

Interference Reactions

Au (0.1) Pt (1)	Immediate precipitation of gold forms. Later yellow platinum prisms and blades envelope the gold crystals. Not soluble in excess reagent. Good test for both elements.
Au (0.1) Pd (1)	Immediate precipitation of gold forms. Considerably later, brown palladium rhombs and petals envelop gold forms. Good test for both elements. Neither precipitate soluble in excess reagent.
Au (0.1) Rh (1)	Immediate precipitation of gold but forms are small and mostly needles. Practically no trace of rhodium until drop dries. Rhodium forms soluble in excess reagent.
Au (0.1) Ru (1)	Immediate precipitation of gold forms. Much later good green ruthenium rhombs and petals envelop gold crystals. Strong test for both elements; neither precipitate is soluble in excess reagent.
Au (0.1) Ir (1)	Immediate precipitation of gold forms. Just before drop dries, a few yellow and green cubes and crosses indicate iridium. These are soluble in excess reagent.
Au (0.1) Os (1)	Immediate precipitation of gold forms. Slowly get yellow osmium cubes, rhombs, prisms and needles. Strong test for both elements; neither precipitate is soluble in excess reagent.

THIOUREA

Individual Reactions

1 per cent
solution

Platinum	Thin yellow petals and rhombs, moderate index of refraction, low birefringence, slowly form. Then jagged prisms grow, dark in D.L., brick red in R.L. Still later long spines grow across drop; dark in D.L., faint yellow in R.L. These usually form just before drop dries.
Palladium	Immediate strong precipitation of fine grained, chocolate brown to black aggregate, followed by very feathery blades and needles that range from light yellow-green to deep yellow in color, high index of refraction, high birefringence. Yellow to pinkish brown in R.L. Strong test. Color of solution changes on addition of thiourea from brown to yellow. Heating the drop dissolves all the precipitate, but it forms again with slow cooling. Rapid cooling gives radiating clusters of (thiourea?) needles stained yellow.
Rhodium	Fairly rapid precipitation of feathery crosses and rosettes of faint to strong yellow color. Very low index of refraction, isotropic. On drying, pink blades

- form at edge of drop. Fairly strong test. Gentle heating changes the solution from pinkish to yellowish orange.
- Ruthenium No precipitate. Cold drop very slowly develops a deep inky blue color. As drop dries, blue-black spherules form at edge of drop. If drop is gently heated after thiourea is added, it immediately turns inky blue. Strong, positive test.
- Iridium No precipitate. No color change in cold or hot solution.
- Osmium No precipitate. Cold drop dries to give thiourea blades stained yellow. Gently heated drop after addition of thiourea gives an immediate change to a reddish purple. Very distinctive test.
- Gold Immediate precipitate of blue black grains, soluble in excess thiourea. As drop evaporates, colorless rhombs and petals form at edge, low birefringence. Still later prisms appear with a high birefringence.

Interference Reactions

- Ruthenium
- Ru (0.1) Pt (1) Warmed—Faint but distinct greenish blue color, blue green on drying, green in R.L. No precipitate of platinum forms.
- Ru (1) Pt (1) Warmed—Strong blue color.
- Ru (0.1) Pd (1) Cold—Solution turns yellow and gives yellow feathery blades and needles of palladium test.
Warmed—Solution turns greenish blue and forms a few blue spherules on cooling. Test for ruthenium distinct but not striking.
- Ru (1) Pd (1) Cold—Strong test for palladium. Later get blue spherules. Drop dries greenish-blue.
Warmed—Solution turns intense blue-green, dries blue-green.
- Ru (0.1) Rh (1) Cold—Light yellow, feathery crosses and clusters of petals slowly form. Good ruthenium test.
Warmed—Solution turns intense blue green.
- Ru (0.1) Ir (1) Cold—No precipitate, drop slowly loses all color.
Warmed—Solution turns intense blue. Dries blue.
- Ru (0.1) Os (1) Cold—No precipitate. Drop remains yellow and slowly develops a few blue spherules. If dry drop is heated it first turns blue and then purple. Strong heating turns it black.
Warmed—Drop first turns blue, then purple to red. Dries reddish purple.
- Ru (0.1) Au (1) Cold—Immediate purple gold precipitate which dissolves, leaving solution with a faint blue color.
Warm—Strong blue ruthenium color, disappears with overheating.
- Osmium
- Os (0.1) Pt (1) Cold—No precipitate, no color change.
Warmed—Drop evaporates to a yellow residue which on stronger heating turns intense pink.
- Os (0.1) Pd (1) Cold—Solution turns greenish yellow, followed by heavy precipitate of palladium forms.
Warmed—Palladium forms dissolve, then reprecipitate as drop dries. Dry drop is yellow, strong heating turns it black. No osmium test.
- Os (1) Pd (1) Cold—See above.
Warmed—Drop turns pink as it dries, continued heating turns it dark red, then black. Satisfactory osmium test.
- Os (0.1) Rh (1) Cold—Slowly, abundant light yellow feathery crosses appear. Drop retains a faint pink color.

- Warmed—Solution turns orange color, dries orange. Rhodium and thiourea when evaporated to dryness give a residue colored a faint yellow-orange.
- Os (1) Rh (1) Warmed—Solution turns reddish purple, dries purple.
- Os (0.1) Ru (1) Warmed—Solution turns blue, then purple.
- Os (0.1) Ir (1) Cold—No precipitate, no color change.
Warmed—Solution turns pink.
- Os (0.1) Au (1) Cold—Gold precipitate forms and redissolves leaving a colorless solution.
Warm—Strong pink osmium color.

MISCELLANEOUS

- Pd (0.1) Cold—Distinct canary yellow color, precipitation of feathery yellow crosses.
- Rh (1) Very weak precipitate of feathery yellow crosses, solution is pink in cold, changes to yellow on warming.
- Pd (0.1) Rh (1) Cold—Solution immediately turns canary yellow and rapid precipitation of many feathery yellow crosses. Color of solution clearly proves presence of palladium.
- Ir (1) No precipitate with thiourea, add ammonium bichromate—immediate fine grained black precipitate plus green clusters and radiating needles as drop dries.
Thiourea plus ammonium bichromate—No precipitate.

TABLE 2. SUMMARY OF TESTS FOR PRECIOUS METAL ELEMENTS

Element	Test	Distinctive in ten times as much of	Distinctive in equal proportions of	Not distinctive in presence of
Platinum	Benzidine Potassium Iodide	Pd, Rh, Ru, Os, Au Ir, Rh, Ru		Ir Pd, Os, Au
Palladium	Dimethylglyoxime plus conc. HCl Thiourea	Pt, Rh, Ru, Ir, Os, Au Pt, Ir, Rh, Ru, Os, Au		
Rhodium	Dimethylglyoxime Benzidine	Pt, Ir, Os, Ru Ir, Au	Pt, Pd, Os	Pd, Au Ru
Ruthenium	Thiourea Rhodanine	Pt, Rh, Ir, Os, Au Pt, Ir, Os	Pd Au	Pd, Rh
Osmium	Thiourea Benzidine Ammonium bichromate	Pt, Ir, Au Rh, Au	Pd, Rh, Ru Pd, Rh, Ru, Au	Pt, Ir Pt, Pd, Ir, Ru
Iridium	Ammonium chloride Potassium bichromate	Pd, Rh, Ru, Au Pd, Rh, Ru, Au	Pt, Os Pt, Os	
Gold	Pyridine in HBr	Pt, Pd, Rh, Ru, Ir, Os		

RECOMMENDED TESTS

Platinum: The benzidine test gives satisfactory results in the presence of any of the precious elements except iridium. In the presence of iridium, the test is sometimes satisfactory but often all that is obtained is an aggregate of small, shapeless grains with no diagnostic features. Potassium mercuric thiocyanate or potassium iodide will give a distinctive platinum precipitate in the presence of iridium. Iridium can be identified in the presence of platinum, and the remainder of the group, except ruthenium, by first adding KI or potassium mercuric thiocyanate to the drop, filtering and then precipitating the iridium with either benzidine or ammonium bichromate.

Palladium: The dimethylglyoxime test for palladium is both sensitive and diagnostic in the presence of any of the elements considered, providing the test drop is strongly acidified with concentrated HCl. A drop of acid as large as the test drop is sufficient to prevent the precipitation of rhodium or gold glyoxime. In weakly acid or neutral solutions the rhodium and gold glyoximes cannot be distinguished from that of palladium.

Rhodium: Rhodium can be identified in the presence of platinum, iridium, osmium and ruthenium by dimethylglyoxime added to a neutral or weakly acidic solution. Palladium and gold will also be precipitated. A drop of concentrated HCl added to the precipitate, will dissolve the rhodium glyoxime readily, the gold slowly, and the palladium glyoxime not at all. Benzidine will give a distinctive test for rhodium in the presence of gold and iridium. The existence of rhodium in the presence of palladium can be confirmed by first precipitating the palladium with dimethylglyoxime in a solution strongly acidified with HCl solution, filtering and testing for rhodium with benzidine. The precipitate is slow in forming but a good test can be obtained with one tenth per cent of rhodium.

Ruthenium: Thiourea gives a satisfactory test for ruthenium in the presence of any of the group except palladium and possibly osmium. An experienced observer can recognize the ruthenium test in the presence of osmium but the blue ruthenium color is quickly replaced by the red osmium color test. Rhodanine gives a satisfactory ruthenium test in the presence of osmium. If palladium is present, it can be removed with dimethylglyoxime, the solution filtered and ruthenium tested for with either thiourea or rhodanine.

Osmium: Platinum, iridium and gold do not interfere with the thiourea test for osmium, but palladium, rhodium and ruthenium prevent a satisfactory test on one tenth per cent osmium solution when they are present in proportions of one per cent or greater. If the concentration

of osmium is equal to that of these elements, the test is satisfactory. Palladium can be first removed by dimethylglyoxime. Ammonium chloride will give a good osmium test in the presence of ruthenium. Ammonium bichromate or ammonium chloride will prove osmium in the presence of rhodium.

Iridium: Iridium is the most difficult of this group of elements to easily identify, since with most reagents it gives a poorly formed precipitate or no precipitate. Ammonium chloride or ammonium bichromate give a good iridium test in the presence of all these elements except platinum and osmium. If either platinum or osmium are present, they must first be removed by precipitation with potassium iodide, the drop filtered and iridium precipitated by either benzidine or ammonium bichromate.

Gold: The pyridine test for gold is entirely satisfactory in the presence of any of the other precious elements. Moreover, several of the other elements slowly give good tests also with pyridine, but since the gold test forms immediately there is no interference.

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Contribution No. 235.