The end-point may be determined electrometrically, or visually if the solution is colorless. In the former case the titration may be made at room temperature if the concentration of hydrochloric acid present is high or at temperatures up to 60° if the concentration of hydrochloric acid is decreased. Above 60° the end-point break is usually unsatisfactory. For the visual end-point the most satisfactory conditions are low concentration of hydrochloric acid and a temperature of 80° or higher.

2. Results obtained by this method and by the bromate titration method of Zintl and Rienäcker agree very closely.

3. Fe^{+++}, Cu^{++}, Bi^{+++}, Cd^{++}, Pb^{++}, Sn^{4+}, Hg^{++}, Zn^{++}, SeO_3^{--}, TeO_3^{--}, AsO_4^{---}, Sb^{5+} and Cr^{+++} are without effect.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BUCKNELL UNIVERSITY]

THE QUANTITATIVE DETERMINATION OF OSMIUM BY MEANS OF STRYCHNINE SULFATE[1]

BY S. C. OGBURN, JR., AND L. F. MILLER

RECEIVED JUNE 28, 1929 PUBLISHED JANUARY 8, 1930

The analytical separations of osmium and ruthenium from the other metals of the platinum group have been based largely on the volatility of their tetroxides from acid and alkaline solutions, respectively. The use of certain organic complexes in the formation of stable coördinated salts with the metals of this group is well known and in some cases they have been used to effect their quantitative removal.[2] Those of the oximes, aromatic nitrosoamines and hydroxyquinolines are especially useful in this connection with platinum and palladium, and 6-nitroquinoline has recently been added to the list as a quantitative reagent for palladium.[3]

In studying the analytical reactions of the platinum metals, one of us[2] found that when a saturated aqueous solution of strychnine sulfate was added to a slightly acidulated solution of sodium chlorosmate, a heavy canary-yellow precipitate was produced, which on settling left a clear supernatant liquid which gave no test for osmium with hydrogen sulfide on boiling, nor with thiourea—a test which will detect one part of osmium in one hundred thousand parts of solution. Following this evidence, the work upon which this paper is based was started with the view of determining whether or not this reagent could be used as a means of quantitatively separating osmium from solutions of its pure salts or from mix-

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[1] This paper is based upon a thesis submitted by L. F. Miller to the Faculty of Bucknell University in partial fulfilment of the requirements for the degree of Master of Science in Chemistry.

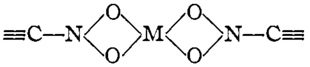
[2] Ogburn, THIS JOURNAL, **48**, 2493 (1926), and other references given therein; also, Ogburn, *ibid.*, **48**, 2507 (1926).

[3] Ogburn and Riesmeyer, *ibid.*, **50**, 3018 (1928).

tures of osmium with the other metals of the platinum group. After some preliminary work was carried out in treating solutions of each of these metals which contained one milligram of metal per cubic centimeter of solution, it was found that in every case a precipitate was obtained with the strychnine sulfate solution. In the case of ruthenium, however, it was found that due to differences in the solubilities of the precipitate obtained with that of the osmium, in ethyl alcohol, a separation of these two metals could be effected, as will be shown later in the paper.

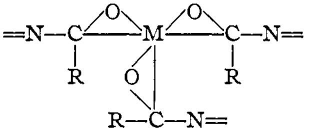
Although the empirical formula of strychnine, $C_{21}H_{22}O_2N_2$, is well known, its constitution is still a subject of some doubt. Perkin and Robinson[4] have stated that within the molecule there must be a quinoline nucleus which probably contains a benzene ring and, since carbazole is formed on reduction with zinc, there must be a carbazole nucleus.

In the case of hydroxyquinolines forming coördinated salts with metals, Bargallini and Bellucci[5] state that the condition is $\equiv C-O-M-N=$ where M is one metallic equivalent and in which the ring is closed by a secondary valence. In the case of 6-nitroquinoline with palladium,[3] the structural condition is



$$\equiv C-N\overset{O}{\underset{O}{\langle\rangle}}M\overset{O}{\underset{O}{\langle\rangle}}N-C\equiv$$

As will be shown in this paper, the osmium salt formed with strychnine is not an additive or double salt but a true coördinated one in which the structural condition is



The stability of this salt lends itself to the quantitative separation of osmium from solutions of its pure salts, and in making use of the differences in solubility in ethyl alcohol of this salt and the corresponding ruthenium one, and in the absence of the other metals of the group, a clear cut separation is effected.

Experimental Part

Preparation of Solutions. (a) The Sodium Chlorosmate Solution.—Several sealed tubes containing one gram each of pure crystalline osmium tetroxide were broken beneath the surface of a 10% solution of sodium hydroxide to which sufficient ethyl alcohol was subsequently added to produce the slight reducing action necessary to cause the formation of sodium osmate. This clear rich red solution was then treated with an excess of concentrated hydrochloric acid and heated to the boiling point. This is necessary to change any osmyl chloride to the sodium chlorosmate form. This greenish to golden yellow solution was diluted, filtered into a glass-stoppered bottle

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[4] Perkin and Robinson, *J. Chem. Soc.*, **97**, 309 (1910).

[5] Bargallini and Bellucci, *Gazz. chim. ital.*, **53**, 605 (1923).

and kept in a cool dark place. In this form the solution is stable for several weeks, as analyses showed. Before using this solution, however, for any quantitative work it was analyzed. This analysis consisted simply in treating a known volume of the chlorosmate solution with previously determined C. P. zinc until all of the osmium was completely reduced to the metallic condition. Carefully prepared Gooch crucibles were used to contain the metal during the washing and drying operations. The analyses ran as follows

Weight of metallic osmium, g.	0.0073	0.0073	0.0072
Amount of solution used, cc.	4.0	4.0	4.0

(b) **The Strychnine Sulfate Solution.**—A saturated solution of this reagent was prepared at room temperature, and contained 3.2% of the salt.

Preparation of the Osmium Compound and the Determination of its Empirical Formula.—Approximately 135 cc. of the sodium chlorosmate solution was treated with an excess of the saturated strychnine sulfate solution. The heavy canary-yellow precipitate was immediately formed and after warming on a water-bath for a few minutes to aid in its coagulation, it was filtered through finely pored paper and washed well to remove chlorides. It was then dried in the usual manner and preserved in a desiccator. The filtrate was free from osmium, as shown by the negative tests given with such reagents as thiourea, hydrogen sulfide and zinc dust.

An analysis of the yellow compound was then made which included determinations for osmium, carbon and hydrogen. The carbon and hydrogen were determined by the usual organic combustion[6] method in which complete oxidation of the compound was attained with the formation of carbon dioxide, water and some osmium tetroxide. In the soda-lime tube of the combustion train some absorption of the volatile osmium tetroxide occurred with the formation of sodium osmate. After weighing, the quantity of osmium absorbed was determined and this amount was deducted in order to obtain the true value of carbon dioxide retained. Approximately 0.2-g. samples were used. About ten such determinations were made. Typical analyses ran as follows

Weight of sample, g.	0.1500	0.1500	0.2000	
Weight of water, g.	.0737	.0797	.0997	
Wt. of carbon dioxide, corr., g.	.3330	.3306	.4180	
Hydrogen, %	5.51	5.94	5.58	Mean value, 5.67
Carbon, %	60.54	60.10	57.00	Mean value, 59.21

The osmium content of the compound was determined by complete oxidation of the osmium in the sample and the subsequent absorption of the volatile tetroxide in 20% sodium hydroxide to which a small quantity of alcohol had been added to aid in the complete conversion to sodium osmate.

The oxidation process was carried out in an oxygen combustion train in which pure dry oxygen was slowly admitted to a transparent vitreosil combustion tube into whose outlet end was sealed, by means of asbestos cement, the entrance end of a wash bottle containing the alcoholic sodium hydroxide solution.

After prolonged preliminary heating, during which all of the volatile matter from the cement was driven off and each connection tested, the determinations were made. When all of the original sample had been completely volatilized, the temperature was maintained at a red heat for about five minutes. After cooling, the contents of the wash bottle was treated with an excess of concentrated hydrochloric acid, diluted and

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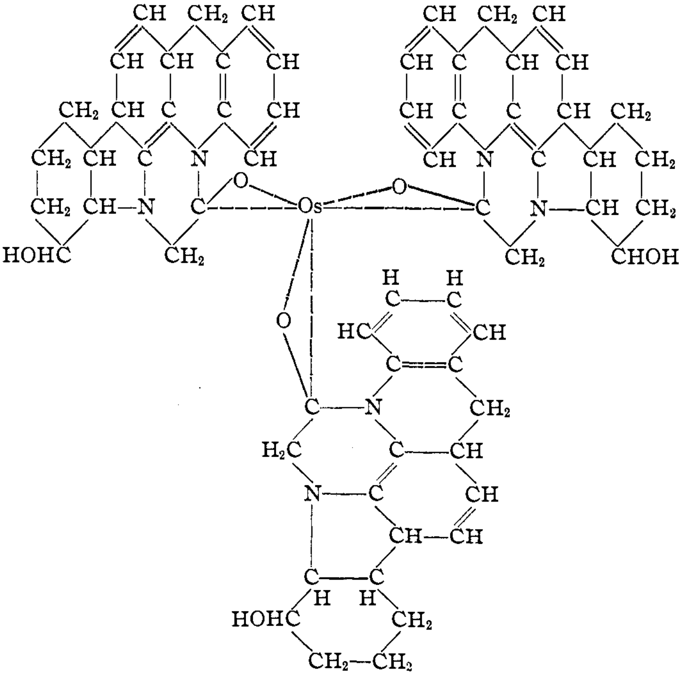
[6] See Clark, "A Handbook of Organic Analysis," 2d. ed., Edward Arnold, London, England, pp. 191–198.

treated with zinc. After complete reduction of the osmium had taken place, it was washed free from chlorides, dried and weighed. Considering the small amount of osmium in the sample taken, these determinations gave very good checks.

Weight of sample, g.	0.2000	0.2000	0.2000	
Weight of osmium recovered, g.	0.0354	0.0351	0.0350	
Oxmium, %	17.70	17.55	17.50	Mean value, 17.58

In order to ascertain whether this compound was a simple additive one, tests were made for the chloride and the sulfate ions on a solution of it in nitric acid. As neither ion was detected, the existence of a coördinated salt was indicated.

Two types of coördination were considered: the one in which the osmium replaces hydrogen and in which the ring is closed by a secondary valence as suggested by Bargallini and Bellucci in the case of hydroxyquinolines, and the other, in which the osmium links with the carbonyl group, forming a conjugated ring system shown in the fore part of this paper. This latter type of linkage is comparable with the structural condition shown in the palladium compound[3] previously described and also with Lowry's[7] study of factors influencing coördination and the use of coördination compounds in analysis. In this paper he states that "the stability of the coördination complex depends largely on the formation of a conjugated ring system in which the metallic ion M acts as a member of a pseudo-aromatic ring."



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[7] Lowry, *J. Soc. Chem. Ind.*, **42**, 462 (1923).

By inspection it will be found that the mean values of the analysis of the yellow osmium compound agree rather closely with the calculated analysis of the compound $(C_{21}H_{22}O_2N_2)_3Os$ in which the osmium exhibits a coördination number of six. In this case the osmium forms a conjugated ring system with the carbonyl group of the strychnine by sharing two pairs of electrons with each three molecules of strychnine. This configuration is represented graphically as indicated.

The osmium atom, with an atomic number of seventy-six, contains two, plus eight, plus eight, plus eighteen, plus eighteen, plus twenty-two electrons in the successive shells. The tetravalent osmium ion, as in the salt sodium chlorosmate used, therefore, contains eighteen electrons in the outer shell, and requires fourteen more to complete the shell of thirty-two. By drawing into this shell one pair of electrons in each of three atoms of oxygen and three atoms of carbon, the osmium coördination number of six is satisfied but there remains a deficiency of two electrons to complete the outer shell, thus rendering the compound stable to the maximum extent. This deficiency, however, is permissible with the formation of stable salts as ascertained by Lowry[8] in which he states that "this shortage of electrons is, however, tolerated much more readily than a surplus as is indeed indicated by the fact that a shortage of three, two and one electrons, respectively, is found in the coördinated compounds, $K_3(Cr{\cdot}6CN)$, $K_2(Pt{\cdot}4CN)$ and $K_3(Fe{\cdot}6CN)$."

The Removal of Osmium from a Solution of Sodium Chlorosmate.—After having determined from the analysis of the yellow osmium compound the gravimetric factor of 0.1758 for its osmium content, a series of analyses was made of sodium chlorosmate solutions of known osmium content, to check the accuracy of this factor and to show the ease with which the reagent, strychnine sulfate, could be used for the quantitative estimation of this metal.

The previously prepared osmium solution, having stood for about forty-five days, was slightly decomposed. The solution was filtered and the osmium content determined by means of zinc reduction as previously described. Close checks were obtained for the value 0.0014 g. of osmium per cubic centimeter of solution. It will be recalled that originally this solution analyzed 0.0018 g. per cubic centimeter.

Five cubic centimeter portions of this chlorosmate solution were treated with an excess of strychnine sulfate solution and the resulting canary-yellow compound filtered. After carefully washing with distilled water until free from chlorides, it was dried to 105° in an electric oven, cooled and weighed. The results of three such determinations were found to coincide with the theoretical weight of the precipitate as calculated by use of the gravimetric factor mentioned above.

[8] Lowry, *J. Soc. Chem. Ind.*, **42**, 316 (1923).

	Soln. boiled during pptn.		Soln. pptd. cold.
Sodium chlorosmate used, cc.	5.0	5.0	5.0
Osmium per cc., g.	0.0014	0.0014	0.0014
Total osmium in soln., g.	.0070	.0070	.0070
Actual wt. of osmium ppt., g.	.0402	.0406	.0399
Theoretical wt. of ppt., g.	.0400	.0400	.0400

From these data it is conclusively shown that osmium may be quantitatively removed from solutions of its salts by means of a saturated solution of strychnine sulfate, and by use of the gravimetric factor 0.1758 the percentage of osmium in the original sample may be calculated from the weight of the washed and dried canary-yellow precipitate obtained. It is also shown that the solubility of the precipitate in water up to its boiling point is negligible. Following the preceding work, a 0.0400-g. sample of the precipitate was allowed to stand overnight in 20 cc. of distilled water at room temperature. On analyzing this solution for osmium by the nascent hydrogen reduction method (zinc and hydrochloric acid) no trace of osmium was found. The thiourea test also failed to detect any metal.

The Separation of Osmium from Ruthenium.—Strychnine sulfate gives with a slightly acidulated solution of ruthenium trichloride a yellow precipitate which is partially soluble on boiling. In no case is this precipitation complete. In the experimental work on the separation of the precipitates obtained by the use of this reagent on solutions containing both osmium and ruthenium, numerous solvents were tried under varying conditions in an effort to effect a complete separation of the osmium compound. Of these, ethyl alcohol was found effective as a means to this end.

A solution containing 0.0014 g. of osmium and 0.0016 g. of ruthenium in soluble form (sodium chlorosmate and ruthenium trichloride) was treated with a small excess of the saturated solution of strychnine sulfate. Immediate precipitation followed. An equal volume of 95% ethyl alcohol was then added and the mixture boiled until the precipitates dissolved. Upon cooling, the osmium compound reprecipitated and after standing for one and one-half hours, it was filtered.[9] The filtrate gave no test for osmium with β-naphthalamine hydrochloride.[10] The results of these determinations were:

Weight of osmium, g.	0.0014	0.0014
Weight of osmium precipitate, g.	.0076	.0078
Theoretical weight of precipitate, g.	.0080	.0080

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[9] Preliminary tests showed no contamination of this precipitate by the ruthenium compound. The latter remained in solution, on cooling, for a period of several days.

[10] The test with thiourea or other usual reagents for osmium cannot be used in the presence of ruthenium. The blue color produced by the reaction of the β-naphthylamine hydrochloride with osmium is a delicate and characteristic test which can be used in the presence of ruthenium. See Ref. 2.

Due to the small quantities of metals used, these small deviations may be regarded as within the limits of experimental error. Such determinations show that osmium may be removed quantitatively from a mixture containing one of its salts with that of ruthenium by means of strychnine sulfate.

Summary

A new quantitative method for the determination of osmium is given. The metal is removed from a solution of sodium chlorosmate by means of a saturated aqueous solution of strychnine sulfate. The composition of the compound formed was found to be $(C_{21}H_{22}O_2N_2)_3Os$, a coördinated salt in which osmium exhibits a coördination number of six. By use of the gravimetric factor, 0.1758, the percentage content of the osmium may be obtained from a direct weighing of the canary-yellow precipitate.

Strychnine sulfate reacts with the formation of precipitates with all of the platinum metals, but the precipitate formed with ruthenium is soluble in boiling ethyl alcohol, from which it does not easily separate on cooling even after a period of several days. This method may be used in effecting a separation of osmium from ruthenium since the former compound reprecipitates completely on cooling the alcoholic solution.

LEWISBURG, PENNSYLVANIA

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 224]

THE HIGH-TEMPERATURE EQUILIBRIUM BETWEEN SILICON NITRIDE, SILICON AND NITROGEN

BY W. B. HINCKE AND L. R. BRANTLEY

RECEIVED JULY 6, 1929 PUBLISHED JANUARY 8, 1930

Plan of the Investigation

This investigation is a continuation of the researches in progress in this Laboratory on high-temperature equilibria.[1] The method devised by Prescott and used by Prescott and Hincke[1d] in studying the equilibrium of the system aluminum carbide, nitrogen, aluminum nitride and carbon was employed. This method consists in heating by an electric current to various temperatures (measured by an optical pyrometer) the solid reaction mixture (in this case the silicon nitride and silicon) within a graphite tube a few millimeters in diameter and a few centimeters long placed within a pyrex bulb, and in measuring the pressures produced. In this article are described measurements made of the dissociation pressures of silicon nitride from 0.27 to 5.49 mm. through a temperature range from 1606 to 1802°K.

[1] (a) Prescott, THIS JOURNAL, **48**, 2534 (1926); (b) Prescott and Hincke, *ibid.*, **49**, 2744 (1927); (c) Prescott and Hincke, *ibid.*, **49**, 2753 (1927); (d) Prescott and Hincke *ibid.*, **50**, 3228 (1928); (e) Prescott, *ibid.*, **50**, 3237 (1928); (f) Prescott and Hincke, *Phys. Rev.*, **31**, 130 (1928).