a mixture of 2 parts of 0.1% pinachrom and 1 part of 0.1% malachite green (or methylene green). At $P_H = 6.0$ the color is green; at $P_H = 7.0$ and 7.2, blue; at P_H 7.4, violet; at 7.6 red-violet. The application of this mixed indicator does not give many advantages.

Summary

1. Pinachrom is an excellent one color indicator for the determination of P_H between 5.8 and 7.8. $PK_h = 7.34 + 0.013\,(20° - t)$.

It is recommended for the determinations of P_H in tap water and distilled water.

2. The salt error at low electrolyte content is negligibly small; at higher salt concentrations pinachrom indicates a too acid reaction.

3. A simple test is described by which the adsorption of a substance at the interface water–air, and the increased concentration of the capillary active substance in this interface can be shown.

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THE REDUCTION OF COLUMBIC ACID. I

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Introduction and History

The investigation of columbium and tantalum-bearing minerals began in 1801 when Hatchett,[1] in a black mineral from Massachusetts, afterwards named Columbite, found a new metallic oxide, "Columbium oxide." About the same time Ekeberg,[2] in a similar mineral from Kimit in Finland, called Tantalite, and in another from Ytterby in Sweden, named Yttrotantalite, detected a new oxide called "Tantalum oxide."

Due to the very close similarity in the chemical behavior of columbic and tantalic acids, and their frequent occurrence together in minerals, there existed up to the year 1865 considerable doubt as to the existence of more than one acid. Some believed them to be identical, while others attributed the observed differences in respective properties to the presence of two other elements, "Pelopium" and "Dianium."

It was not until 1865 that the compositions of columbite and tantalite were established. Marignac,[3] then, in his classic researches on columbium and its compounds, proved conclusively that all columbites and tantalites contained columbic and tantalic acids. Since that time, by far the greater part of the work done on columbium concerned either the prepara-

[1] Hatchett, *Phil. Trans. Roy. Soc.*, **92,** 49 (1802).

[2] Ekeberg, *Ann. chim.*, **43,** 276 (1803).

[3] (a) Marignac, *Ann. chim. phys.*, [4] **8,** 1 (1865); (b) [4] **8,** 49 (1865).

tion of compounds or the analytical separation of it from tantalum and other associated elements.

Columbic acid unlike tantalic acid gives upon reduction with zinc and mineral acids blue solutions. This color change attracted the attention of a number of investigators, among the earlier of whom were Wöhler,[4] Nordenskjöld,[5] Rose,[6] Blomstrand[7] and Marignac.[8] Although these researches produced nothing definite so far as the chemistry of columbium was concerned, except the obtaining of these colored solutions, yet they furnished a basis upon which the volumetric methods of Osborne,[9] Levy,[10] Giles[11] and Metzger and Taylor[12] were developed and proposed to replace the tedious gravimetric procedure of Marignac,[3] which at best was limited to an accuracy of plus or minus one part in one hundred. Both speed and accuracy were claimed for the above methods. Recently, however, Schoeller and Waterhouse[13] questioned the reliability of these volumetric methods because the results depended upon empirical factors rather than stoichiometric relations. They claim that the values of these factors will vary with the slightest alteration of the experimental conditions upon which the extent of reduction depends and the determinations are fundamentally based.

Osborne[9] in his work states that with acids of low concentration zinc yields a blue solution and that with acids of high concentration a brown solution is obtained. Metzger and Taylor observed that with zinc in hot dilute sulfuric acid solutions of columbium, a blue color is first obtained which rapidly changes to brown. Although attempts were made by some of the above earlier investigators to isolate the reduction products, their efforts were unsuccessful.

In 1896 Pennington,[14] in an endeavor to devise a separation of columbium from titanium, subjected an aqueous solution of $2KF\cdot CbOF_3\cdot H_2O$ to electrolysis and obtained a blue precipitate which was probably a lower hydrated oxide of columbium. No attempt, however, was made to determine its composition.

The electrolytic reduction of columbium pentachloride in concentrated sulfuric and hydrochloric acids was investigated by Ott[15] while he was

[4] Wöhler, *Ann. Pogg.*, **48,** 93 (1839).

[5] Nordenskjöld, Gmelin-Kraut, Carl Winter, Heidelberg, **1928,** Vol. VI (1), p. 219.

[6] Rose, *Ann. chim. phys.*, *Pogg.*, **112,** 475 (1860).

[7] Blomstrand, Gmelin-Kraut, Carl Winter, Heidelberg, **1928,** Vol. VI (1), p. 220.

[8] Marignac, *Ann. chim. phys.*, [4] **13,** 30 (1867).

[9] Osborne, *Am. J. Sci.*, [3] **30,** 331 (1885).

[10] Levy, *Analyst*, **40,** 204 (1905).

[11] (a) Giles, *Chem. News*, **95,** 1 (1907); (b) **99,** **1** (1909).

[12] Metzger and Taylor, *J. Soc. Chem. Ind.*, **28,** 818 (1909).

[13] Schoeller and Waterhouse, *Analyst*, **49,** 215 (1924).

[14] Pennington, THIS JOURNAL, **18,** 67 (1896).

[15] Ott, *Z. Electrochem.*, **18,** 349 (1912).

attempting to prepare compounds containing trivalent columbium. He found that when columbium pentachloride was reduced in concentrated hydrochloric or sulfuric acid or in an alcoholic solution of anhydrous hydrogen chloride, reddish-brown to black solutions were obtained which he stated contained trivalent columbium. Sodium columbate in an hydrochloric acid solution yielded on reduction a green solution which, as he observed, contained quadrivalent columbium. Fused K_2CbOF_3 yielded on electrolytic reduction a bluish-black product which also seemed to contain quadrivalent columbium. When columbium pentachloride was reduced in concentrated sulfuric acid at a platinum cathode, a blue solution was obtained which appeared to contain a compound of tetravalent and pentavalent columbium corresponding to the oxide Cb_3O_7 or $Cb_2O_5{\cdot}CbO_2$. No definite solid compounds, moreover, could be isolated from the hydrochloric acid solutions; but from the concentrated sulfuric acid solution, in the presence of ammonium sulfate, reddish-brown crystals were obtained which had the probable composition indicated by the formula $Cb_2(SO_4)_3{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$. These crystals, however, could not be quite freed from adhering sulfuric acid. The sulfuric acid solutions of columbium pentachloride employed by Ott throughout his investigation contained approximately 1% of columbium and about 85% of sulfuric acid. No variation of concentration was made nor were experiments performed with solutions of pure columbic acid in sulfuric acid.

Furthermore, in an extended review of the literature, no work was found which furnished definite fundamental information concerning the reduction of columbic acid under conditions whereby the influencing factors were studied and the chemical relations established.

Accordingly, therefore, a research on the reduction of columbic acid was planned and the results given below furnish information on the following points: (a) the solubility of columbic acid in sulfuric acid; (b) the most favorable conditions for preparing a stable and relatively concentrated solution of columbic acid in sulfuric acid; (c) the conditions under which the pentavalent columbium in solution (b) can best be reduced to trivalent columbium.

Experimental

Chemicals.—All chemicals employed throughout this investigation were of the purest grade obtainable. They were further treated by recrystallization from water or by other suitable means of purification, when essential to the purity of the final product.

Columbic Acid.—It was practically impossible to obtain a grade of columbic acid of sufficient purity to warrant its use in this research; so the mineral columbite, which is the most plentiful source of columbium, was used as the starting material for the preparation of pure columbic acid. Because of its importance in this investigation, the method of preparation will be outlined below.

The mineral was first subjected to a qualitative and a partially quantitative analysis to determine approximately the composition. Fifty-three per cent. of Cb_2O_5, 21% of

Ta_2O_5, together with FeO and MnO and small quantities of TiO_2, SiO_2 and SnO_2 were found.

The preparation of pure columbic acid may be divided into two parts.

(a) **The Preparation of K_2CbF_7.**—The procedure followed was that described by Hall and Smith[16] with certain modifications designed to improve the manipulations. This procedure, which is a further modification of the original method proposed by Marignac, is based upon the different solubilities of potassium fluotantalate and the corresponding columbium compound. Five kilograms of the mineral columbite, ground to 150-mesh, were fused in 100-g. lots with potassium pyrosulfate. Each fusion was made in a large platinum dish, as follows: 400 g. of potassium pyrosulfate was melted in the platinum dish and 100 g. of the finely powdered mineral was added slowly in small portions. Each portion was allowed to fuse completely before the next was added. The melted mass was stirred with a platinum rod. This part of the procedure consumed approximately two hours before all of the mineral was added and a clear and quiet fusion was obtained. After the dish was cooled and the melt was removed, the operation was repeated.

When the fusions were completed the combined melts, broken into small pieces, were digested in distilled water for several days to effect complete disintegration. Mechanical stirrers were used to keep the mixture well agitated. From time to time the precipitated impure columbic and tantalic acids were allowed to settle so that the supernatant liquid could be replaced by distilled water. By this procedure most of the titanium, the most difficult element to separate from columbium, and tantalum were removed together with other impurities which went into solution.

After several days of the preceding treatment, the supernatant liquid was replaced by a molar solution of ammonium sulfide and mechanically stirred for several days. Then the ammonium sulfide solution was removed and the precipitated columbic and tantalic acids were washed alternately with dilute ammonium hydroxide and molar sulfuric acid till the washings were free from iron by the ferrocyanide test.

Thereupon the precipitated acids were washed on a Büchner funnel with distilled water, transferred to a platinum dish and taken into solution with a 40% hydrofluoric acid solution. After sufficient digestion the acid solution was filtered through ordinary filter paper supported on a hard rubber funnel surrounded by a hot water coil, thereby removing the undecomposed mineral and potassium fluosilicate. To the filtrate in a large hard rubber dish a solution of potassium hydroxide was added to precipitate the less soluble potassium fluotantalate, which was removed by filtration. The potassium fluocolumbate left in the solution was further purified to free it from titanium, tin, tungsten, tantalum, silicon and iron, likely to be present at this point in the process, by a method described below.

(b) **Purification of K_2CbF_7 and its Conversion to Columbic Acid.**—The procedure followed to effect the purification of K_2CbF_7 and the formation of columbic acid was that outlined by Hall and Smith[16] and Balke and Smith.[17]

Four crystallizations from aqueous hydrofluoric acid containing about 20% of the anhydrous acid were sufficient to remove such impurities as tin, tungsten, iron and titanium. The last traces of tantalum were removed by baking the double fluoride as directed by Hall and Smith.[16] The purified double fluoride was dissolved in water in a platinum dish and the solution boiled for several days. K_2CbF_7 was thus changed to $K_2CbOF_5 \cdot H_2O$, which was finally baked for several hours, dissolved in water and filtered through filter paper on a hard rubber funnel surrounded by a hot water jacket. This

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[16] Hall and Smith, THIS JOURNAL, **27,** 1369 (1905).

[17] Balke and Smith, *ibid.*, **30,** 1637 (1908).

operation was repeated until the insoluble residue, when dissolved in hydrofluoric acid, indicated the solubility of potassium fluoxycolumbate. This occurred usually after three treatments.

A possible trace of silica was removed in the conversion of the potassium fluoxycolumbate to columbic acid by heating the $K_2CbOF_5 \cdot H_2O$ with a large excess of concentrated sulfuric acid until very little acid was left. This was necessary to remove all traces of hydrofluoric acid. The solution was then cooled and carefully diluted with distilled water. The resulting mixture was made faintly alkaline with ammonium hydroxide, the excess of which was removed by boiling. The precipitated columbic acid was filtered, washed with distilled water until the washings no longer gave a test for sulfates and then dried in a Freas oven at 50°. The final product was found to contain approximately 17.5% of water. When columbic acid was dried at 100°, we found, as stated generally in the literature, that it retained varying amounts of water, depending upon its physical character.

The method of Balke and Smith[17] for preparing pure columbic acid has been shown to be thoroughly reliable by Barr,[18] who subjected material purified by this method to a spectroscopic analysis. Further confirmation was obtained by Hildebrand[19] through the examination of the arc spectrum of the material.

Solubility of Columbic Acid in Sulfuric Acid

Although it is frequently mentioned in the literature that columbic acid is soluble in concentrated sulfuric acid, nevertheless no results were found to show the extent to which it is soluble. Whereupon, after making a number of preliminary experiments, the following procedure was developed to determine the solubility of columbic acid in sulfuric acid.

Procedure.—In a 400cc. Pyrex beaker approximately 50 g. of columbic acid was treated with 200 cc. of concentrated sulfuric acid.[20] The beaker was covered with a watch glass and the mixture boiled for five minutes, after which it was allowed to cool to 30°. It was then transferred to a 250cc. glass-stoppered bottle and immersed in a Freas thermostat regulated to 25° ±0.01, where it remained for several days. During the interval it was shaken frequently. Then, by means of a pipet, 50cc. portions of the solution were withdrawn and centrifuged at 3000 revolutions per minute until the solutions were perfectly clear. These clear solutions were analyzed for the columbium and sulfate content by the following methods.

Methods of Analysis, (a) Cb_2O_5.—A weighed sample was carefully diluted with 200 cc. of distilled water. Ammonium hydroxide was added until the solution was faintly alkaline, the mixture heated to boiling and the precipitated columbic acid obtained by filtration. The precipitate was then washed with very dilute ammonium hydroxide till the washings failed to give a test for sulfate. The residue was dried, ignited in platinum and weighed as Cb_2O_5. The filtrate and washings were kept for the sulfate determination.

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[18] Barr, THIS JOURNAL, **30**, 1668 (1908).

[19] Hildebrand, *ibid.*, **30**, 1672 (1908).

[20] The concentrated sulfuric acid used throughout this work was of the highest purity obtainable. It contained 95.92% of anhydrous sulfuric acid.

(b) **H_2SO_4**.—The combined filtrate and washings from (a) were acidified with dilute hydrochloric acid and transferred quantitatively to a 500-cc. volumetric flask. The solution was then diluted, with thorough stirring, to the graduation with distilled water. To exactly 50 cc. of this solution was added an excess of a barium chloride solution to precipitate the sulfate which, after standing, was filtered, washed, dried, heated and weighed in the usual quantitative procedure. The results obtained are recorded in Table I.

TABLE I

SOLUBILITY OF COLUMBIC ACID AT 25°

Sample soln., no.	Weight of soln., g.	Cb_2O_5, g.	H_2SO_4, g.	Cb_2O_5, %	H_2SO_4, %	H_2O, by diff., %
1	3.6479	0.3044	3.213	8.34	88.06	3.60
2	3.8005	.3169	3.351	8.34	88.17	3.49
3	4.0174	.3353	3.536	8.35	88.03	3.62
4	3.6742	.3061	3.241	8.33	88.21	3.46
5	3.6396	.3043	3.206	8.36	88.09	3.55
6	3.9341	.3277	3.467	8.33	88.12	3.55
			Average	8.34	88.11	3.55

From Table I it is evident that 8.34 g. of columbium pentoxide is soluble in 100 g. of solution containing 88.11% of anhydrous sulfuric acid. The specific gravity of this solution was determined and found to be 1.85. From this we calculated that 15.43 g. of columbium pentoxide is dissolved in 100 cc. of this solution. For practical purposes, however, it may be concluded that by the above procedure approximately 15 g. of columbium pentoxide will dissolve in 100 cc. of concentrated sulfuric acid.

Similar experiments, which were carried out with columbic acid that had been prepared in the usual way except that it had been successively washed with a mixture of alcohol and water, a mixture of absolute alcohol and ether, finally anhydrous ether previously distilled over sodium and dried in a vacuum desiccator over anhydrous calcium chloride, gave approximately the same results. Analyses of the columbic acid prepared in this way gave a water content of 15.28%.

Preparation of a Solution of Columbic Acid

While determining the solubility of columbic acid in sulfuric acid the separation of a precipitate caused by hydrolysis upon dilution was noticed. When, however, care was taken to keep the solution cool during the dilution, no precipitation occurred with more extended dilution.

This led to experimentation which established the final concentration of sulfuric acid necessary to prevent precipitation from a 0.038 M solution of columbic acid when a hot solution of higher concentration of both sulfuric acid and columbic oxide was cooled in a beaker surrounded by ice and diluted. No precipitation occurred before more than three days had elapsed if the final concentration of sulfuric acid was 3 M or greater. With higher final concentrations of sulfuric acid it was possible to increase the amount of columbic acid which remained in solution. In this investigation a solution of approximately 0.025 M Cb_2O_5 was therefore employed in most of the experiments which follow because it was not deemed advisable to work with a solution which was so near the limit of solubility.

Reduction of Columbic Acid

By Chemical Means.—At the beginning of this paper a brief account of the reduction of columbic acid by a metal in mineral acids was given. After such reductions a blue solution was obtained if the acid used was dilute and a brown solution was obtained if the acid was concentrated. The exact extent of these reductions has not been definitely determined in any case and when a quantitative determination of columbium, based upon such reductions, was made an empirical rather than a stoichiometric factor was found and employed.

The colored solutions have also served to distinguish columbium from tantalum, which remains colorless in the solution. The conditions favorable to the sensitivity, however, have not been given. It was therefore considered worth while to work out the limits of the test and give the conditions most favorable.

Procedure for the Detection of Columbium in the Presence of Tantalum.—The solution to be tested was prepared according to the method described under "Preparation of a Solution of Columbic Acid." To 2 cc. of this solution in a test-tube, 1 cc. of concentrated sulfuric acid and 7 cc. of water were added. A few pieces of mossy zinc (about one gram) were next introduced and the mixture was allowed to react for five minutes. A blue solution proves the presence of columbium.

Sensitivity of the Test.—Under the above conditions it was found that the limit of the test was a 0.00032 molar columbium solution in the presence of a relatively high concentration of tantalum. When such a small quantity of columbium is present in the solution, a very pale green color is observed.

Electrolytic Reduction.—It was pointed out in the introduction that Ott[15] prepared a double salt of trivalent columbium sulfate and ammonium sulfate. This salt is not a very desirable substance from which to prepare pure solutions of trivalent columbium for several reasons. In the first place, it is difficult to free the substance from adhering sulfuric acid. Again, its ease of oxidation by air makes it impracticable to use. Besides, the presence of ammonium sulfate is undesirable in many subsequent experiments where accurate measurements are desired. It was therefore necessary to work out the conditions whereby a solution of trivalent columbium of the least complexity could be prepared which would be suitable for the various physical measurements.

A few preliminary experiments soon proved that very little reduction could be obtained at a platinum cathode. At best only a very pale blue solution was obtained. In order to secure a better reduction, it was therefore necessary to employ as a cathode a metal which possessed a higher hydrogen overvoltage. While Ott[15] used a lead cathode for reducing a solution of columbium pentachloride in concentrated sulfuric acid, it was believed that mercury, which has a much higher hydrogen overvoltage, would be better. Besides, mercury can be readily purified and it is not attacked by sulfuric acid except when the acid is both hot and very concentrated.

Reduction of Columbic Acid at a Mercury Cathode

An arrangement of the apparatus devised for the reduction of columbic acid at a mercury cathode is given in Figure 1. It consists of two wide-mouthed bottles, A and B, each of 1000cc. capacity. A, acting as the cathode, is closed with a rubber stopper pierced with five holes. Through these holes, respectively, pass a glass tube with a sealed-in platinum wire to make contact with the mercury on the bottom of the cell, a glass tube to admit hydrogen, a glass tube to act as a bridge to connect the solution in A to that in B, a glass tube leading into a bottle acting as a water seal to liberate the excess hydrogen and, finally, a narrow glass tube to deliver the reduced solution to a buret by the pressure of hydrogen.

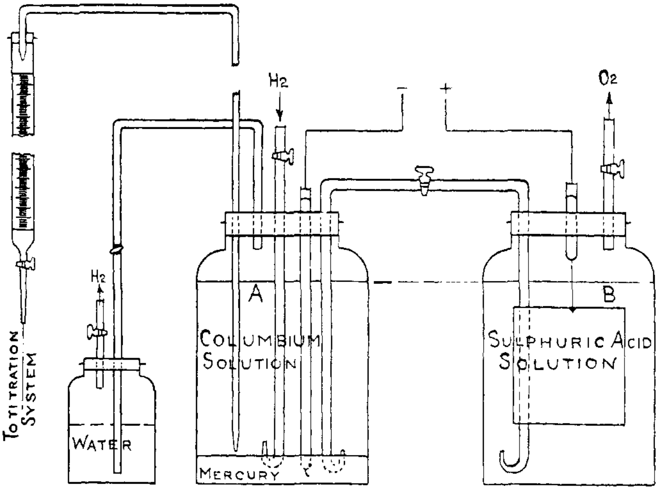

Fig. 1.—Reduction Apparatus.

The bottle B is also provided with a rubber stopper pierced by three holes through which pass, respectively, a glass tube connecting the solution in B with that in A, a glass tube to liberate any gases formed at the anode during the electrolytic reductions and a glass tube with a sealed-in platinum electrode (5 by 8 centimeters) to act as the anode. The bridge connecting A and B was made of glass tubing of 7 mm. internal diameter with openings on either end of 3 mm. diameter. The mercury used throughout this investigation was washed with nitric acid according to the method of Hildebrand.[21] It was filtered through a clean towel and was finally distilled under reduced pressure with access to air as recommended by Hulett.[22]

The bottle A, acting as the mercury cathode, held the columbic acid solution. The bottle B was filled with an equal amount of sulfuric acid of the same molarity as the solution containing the columbium. The two solutions were connected by a bridge, without plugs, filled with the sulfuric acid solution. Hydrogen from a cylinder, purified by passing it successively through alkaline permanganate, alkaline pyrogallol solution, water, cotton wool and finally through some of the same solution used in the process, was passed through the columbium solution during the reduction. The hydrogen, besides furnishing a means to exclude oxygen to which the reduced solution is sensitive, served as a stirrer.

When the arrangement of the apparatus was completed, an electric current whose current density in all reductions was three milliamperes per square centimeter was passed through the system. The progress of the reduction was determined at intervals by adding an excess of an oxygen free standard potassium permanganate solution to a test portion of the reduced solution and by titrating back with a standard ferrous sulfate solution in the following manner.

Since the reduced solution is very susceptible to the action of oxygen, the standard potassium permanganate solution was prepared with boiled distilled water and was kept under an atmosphere of hydrogen, by the pressure of which the potassium permanganate was introduced into the buret connected to the stock solution. From time to time the potassium permanganate solution was standardized against sodium oxalate which had been obtained from the Bureau of Standards. A test portion of the reduced columbium solution was obtained by allowing the pressure of hydrogen to force the solution in A into a buret, from which it was measured into a flask, previously swept by hydrogen and hermetically connected with the potassium permanganate buret, where the titration was made. In this manner the titrations were all carried out in an atmosphere of hydrogen.

The reduction was allowed to proceed until the amount of standard potassium permanganate solution required to oxidize a 25cc. portion of the reduced solution remained constant within experimental error. This point was considered to be the termination of the reduction. In the tables below are listed the data showing the progress and extent of reduc-

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[21] Hildebrand, This Journal, **31**, 933 (1909).

[22] Hulett, *Z. physik. Chem.*, **33**, 611 (1900).

tion of 0.025 *M* columbic acid in 3, 6 and 10 *M* sulfuric acid solutions, respectively.

Upon the basis that columbium is pentavalent in columbic acid and columbium pentoxide, calculations based upon the equivalents of potassium permanganate required for reoxidation to its original condition were made to establish the valence of the reduced state. In all cases whether the reduced solution was blue or brown in color the valence in the reduced form was found to be three. Percentage reduction was determined by comparing the quantity found in the trivalent state to the amount in the original solution. The limiting error in the procedure in all determinations was in the titration of the measured 25cc. portions. This did not at greatest exceed 2 parts per 1000.

TABLE II

REDUCTION AT A MERCURY CATHODE

		0.025 *M* Cb_2O_5		
25 cc. Sample no.	Time of reduction, hours	0.02 *M* $KMnO_4$ required, cc.	Valence of reduced from, calcd.	Columbium required, %
		3 *M* sulfuric acid		
1	4	22.01	...	88.16
2	6	24.66	...	98.77
3	8	24.95	3.004	99.93
4	9	24.93	3.006	99.86
5	10	24.92	3.005	99.82
6	12	24.95	3.004	99.93
Duplicate				
1	4	23.17	...	92.80
2	5	23.70	...	94.92
3	8	24.91	3.007	99.80
4	10	24.95	3.004	99.93
5	12	24.93	3.006	99.86
6	14	24.94	3.005	99.89
Triplicate				
1	4	22.54	...	90.27
2	6	24.73	...	99.04
3	8	24.94	3.005	99.89
4	10	24.91	3.007	99.80
5	12	24.93	3.006	99.86
6	14	24.94	3.005	99.89
		6 *M* sulfuric acid		
1	4	22.37	...	89.59
2	6	24.41	...	97.76
3	8	24.90	3.008	99.72
4	10	24.95	3.004	99.93
5	12	24.91	3.007	99.80
6	13	24.93	3.006	99.86

TABLE II (*Concluded*)

		0.025 M Cb_2O_5		
25 cc. Sample no.	Time of reduction, hours	0.02 M $KMnO_4$ required, cc.	Valence of reduced form, calcd.	Columbium reduced, %
Duplicate run				
1	5	23.05	...	92.31
2	6	24.62	...	98.60
3	8	24.93	3.006	99.86
4	10	24.91	3.007	99.80
5	12	24.94	3.005	99.89
		10 M sulfuric acid		
1	4	18.29	...	73.25
2	6	24.58	...	98.44
3	10	24.81	3.015	99.36
4	12	24.95	3.004	99.93
5	14	24.92	3.006	99.82
6	16	24.93	3.005	99.86
Duplicate run				
1	6	24.25	...	97.12
2	8	24.87	3.010	99.60
3	10	24.92	3.006	99.82
4	12	24.94	3.005	99.89
5	15	24.91	3.007	99.80

As a further check on the reliability of the method of reduction, the total columbium content was quantitatively determined in 25cc. samples of both the unreduced and reduced solutions—before and after reduction, respectively. The results are shown in Table III.

TABLE III

DETERMINATION OF TOTAL COLUMBIUM

	Unreduced Solution		Reduced Solution	
Sample No.	Soln., cc.	Cb_2O_5, g.	Soln., cc.	Cb_2O_5, g.
1	25	0.1664	25	0.1668
2	25	.1667	25	.1663
3	25	.1666	25	.1665

To determine the total columbium content in the reduced solution, hydrogen peroxide was first added to oxidize the columbium. The resulting solution was then evaporated to at least half its volume to destroy the excess of hydrogen peroxide. Ammonium hydroxide was added to make it alkaline and the precipitated columbic acid was determined in the usual manner.

From these experiments we conclude that at a mercury cathode complete reduction to the trivalent state can be obtained, within experimental error, ranging from 99.80 to 99.96% reduction with solutions of columbium in 3 M, 6 M and 10 M sulfuric acid.

Color Changes of the Columbium Solution during Electrolytic Reduction.—In the presence of 3 M sulfuric acid the reduced solution first assumes a blue color which increases in intensity as the reduction is extended. The final solution possesses a very deep blue color and is nearly opaque. Reddish-brown solutions are obtained, however, in the presence of 6 *M* and 10 *M* sulfuric acid. Here also the intensity increases with the extent of the reduction. It was of interest to note that these brown solutions upon dilution became blue. Many attempts were made to isolate a solid compound of trivalent columbium from these reduced solutions but without success.

Effect of Mixing and Dilution on the Reduced Columbium Solutions.—1. Varying amounts of the reduced solutions were severally added to varying amounts of unreduced solution through which hydrogen had been previously passed to remove any traces of oxygen. The resulting mixtures, which were prepared in an atmosphere of hydrogen, were treated with a definite excess of standard potassium permanganate which was titrated back with standard ferrous sulfate. In Table IV are some of the results obtained.

TABLE IV

MIXTURE OF REDUCED AND UNREDUCED SOLUTIONS

Expt. no.	Reduced soln.,	Oxidized soln.,	0.02 *M* $KMnO_4$ req. by undil. soln., cc.	0.02 *M* $KMnO_4$ req. by dil. soln., cc.
1	25	75	24.94	24.92
2	50	50	49.88	49.83
3	75	25	74.82	74.80

Since the amount of potassium permanganate required did not vary, it was evident that no change had taken place as a result of mixing the solutions.

2. Portions of the completely reduced solutions containing 6 *M* and 10 *M* sulfuric acid were diluted carefully, in an atmosphere of hydrogen, with distilled water which had been previously boiled. The brown solutions became blue on dilution. A comparison of the titrations of the diluted solutions with the undiluted revealed no change in the amount of potassium permanganate required. No change of valence had occurred. The valence of the columbium in the brown solution was also three.

It seems from the foregoing experiments that the various colored solutions obtained by the electrolytic reduction of columbic acid in 3, 6 and 10 *M* sulfuric acid are not due to the different valences of columbium in solution, since in each concentration of acid the trivalent state was established on the basis of the permanganate equivalents required, but to some type of complex in the strong sulfuric acid solutions which hydrolyzes or decomposes upon dilution.

Summary

1. The solubility of columbic acid, which had been prepared from the mineral Columbite according to a slightly modified procedure of Hall and

Smith, and Balke and Smith, was determined in concentrated sulfuric acid. A saturated solution was found to contain 8.34 g. of columbium pentoxide and 88.11% anhydrous sulfuric acid in 100 g. of solution.

2. The most favorable conditions were determined for preparing a stable and relatively concentrated solution of columbic acid in sulfuric acid. The solution must contain at least 3 M sulfuric acid and not more than 0.038 M Cb_2O_5 to remain stable for three days. A higher concentration of Cb_2O_5 may be obtained only when the concentration of sulfuric acid is greater than 3 M.

3. A procedure which is sensitive to 0.00032 M columbium solution was devised for the detection of small amounts of columbium in the presence of tantalum.

4. By using mercury, which has a high hydrogen overvoltage as a cathode, solutions of columbic acid containing 3, 6 and 10 M sulfuric acid were completely reduced to the trivalent state within experimental error. The apparatus devised for such reductions has been described.

This will form the basis of a volumetric method for the quantitative determination of columbium, employing a stoichiometric factor, work for which has been planned.

5. In the presence of 3 M sulfuric acid, a blue solution is obtained upon electrolytic reduction, while in 6 M and 10 M sulfuric acid, reddish-brown solutions were formed which became blue on dilution with water. These brown solutions turned blue upon dilution, indicating complex compounds rather than a different valence.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF WESTERN RESERVE UNIVERSITY]

THE DETERMINATION OF TRACES OF MERCURY.

III. THE QUANTITATIVE DETERMINATION OF MERCURY IN URINE AND FECES AND THE INFLUENCE OF MEDICATION[1]

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The method for the quantitative determination of traces of mercury described by Booth, Schreiber and Zwick[2] was intended primarily for the study of the clinical excretion of mercury. The present paper deals with its applicability to urine and feces. These may introduce complications

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[1] This research has been carried on in collaboration with Dr. H. N. Cole of The School of Medicine of Western Reserve University, as a preliminary to a comprehensive study of the absorption and elimination of mercury and mercury compounds by the human body.

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[2] Booth and Schreiber, THIS JOURNAL, **47**, 2625 (1925); Booth, Schreiber and Zwick, *ibid.*, **48**, 1815 (1926).