hours in this acid at 110° C. the total loss of metal was only 0.34% and the surface was still bright.

Sulfuric acid, diluted (sp. gr. 1.30), at 110° does not attack molybdenum. The concentrated acid (sp. gr. 1.82) attacks it but very slowly at this temperature. Only 0.29% loss in weight was found after 18 hours. With elevated temperatures, however (200–250°), the metal dissolves rapidly to a green solution, with the evolution of sulfur dioxide.

Nitric acid, concentrated (sp. gr. 1.40), dissolves molybdenum slowly with the formation of molybdic anhydride, MoO_3, which deposits on the surface of the metal and retards the action. The more dilute acid (sp. gr. 1.15), however, attacks the metal rapidly.

Aqua regia also dissolves the metal rapidly, especially if heated.

Hydrofluoric acid (hot or cold) does not attack molybdenum.

Potassium hydroxide solutions do not attack molybdenum, but it is soluble in the fused alkali.

It will be noted that both of these metals are to a certain extent acid-resisting and this is due principally to the formation of an acid-resisting coating of oxide. Tungsten is attacked most rapidly by fuming sulfuric acid, and this only to the extent of 1.2% in 8 hours.

Molybdenum is much more easily dissolved than tungsten. It resists concentrated hydrochloric and sulfuric acids at moderate temperatures (below 125°) fairly well and is untouched by hydrofluoric acid.

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PERCHLORIC ACID IN ELECTROCHEMICAL ANALYSIS.

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In the latter part of the academic year 1910–'11 the writer made electrolytic separations of certain metals from perchloric acid solution with good results. The pressure of other duties made it necessary to discontinue the work for a time. In the meantime Henryk Golblum[1] has published a paper on the determination of perchloric acid in the perchlorates of nickel and cobalt, his method being to deposit the metals electrolytically and titrate the acid left in solution. Though the determination of the metals was apparently not his object, he states that they were deposited quantitatively, and that the method for the determination of the acid would probably be found applicable in all perchlorates whose metals can be deposited in weak acid solutions. Since these statements seem to foreshadow work in the direction of my own, it seems desirable to publish a brief statement of the work done in this laboratory.

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[1] *Z. anal. Chem.,* 1911, 741.

Several years ago, while studying the action of certain oxidizing acids on metals, the writer became much impressed with the great indifference of perchloric acid in solution toward chemical reagents and especially those of a reducing character. The only reducing agents that are effective seem to be freshly precipitated ferrous oxide, sodium thiosulfate and to a small extent some oxides of nitrogen. Certain other substances decompose it when highly heated with it in sealed tubes. There seems to be no other strong, that is highly dissociated, oxygen holding acid comparable with perchloric acid in the indifference of its negative ion toward such agents, save sulfuric acid, and even this is reduced by hydriodic acid and many other agents that under like circumstances are ineffective toward perchloric acid. In short, in water solution perchloric acid exhibits only the properties due to its primary ions, and there are no side reactions due to the decomposition of its negative ion.

It seems that such a stable and strong acid should find more uses, interesting to the chemist, at least, and possibly of practical importance if cheaper methods could be found for its manufacture. Since the choice of solvents is somewhat restricted in electro-chemical analysis, it occurred to the author that the question of the availability of perchloric acid in this capactity was worthy of study. As anticipated, it was soon found that some metals may be easily and completely deposited in weighable form from perchloric acid solutions; moreover, since the acid is so strong and stable, metals may easily be converted into perchlorates for electrolysis.

Perchloric acid readily dissolves many oxides of the heavy metals. Oxides, metals, or other refractory substances, may also be converted into nitrates with nitric acid, and this acid replaced by evaporation with an excess of perchloric acid. To test this point a known volume of a standard potassium nitrate solution was evaporated on the water bath with an excess of perchloric acid. Water was added and the evaporation was repeated, after which a determination showed that 94% of the combined nitric acid had been replaced. In parallel experiments equal weights of copper were dissolved in nitric acid, and evaporated, one with and the other without the addition of an excess of perchloric acid. Determination of the nitric acid in the residues showed that 98% had been expelled by the perchloric acid. There is no danger of decomposing perchloric acid by evaporation on the water bath, and it is probable that considerably higher temperatures may be used.

To the present time electrolytic determinations of three metals have been made from perchloric acid solution: copper, silver and cadmium.

Copper.

Copper oxide was prepared from pure copper sulfate. After thorough washing it was dried and heated for an hour in a porcelain boat in a current of oxygen. Small portions were weighed in a platinum dish and dissolved in a small excess of pure perchloric acid. The acid showed scarcely a trace of hydrochloric, chloric acid or any other impurity. The solution was made up to 100 cc. with pure water and subjected to the electric current for about three hours. The revolving anode was used. At the beginning the current showed 0.2 ampere to one square decimeter of cathode surface and 2.5 volts; later the current was increased. At the end of each experiment the solution was siphoned off and replaced with water while the current was running, and the free perchloric acid was titrated. Two analyses are as follows:

	Copper oxide.	Calculated copper.	Copper found.	Acidity.
1...........	0.3011	0.2405	0.2407	0.1 *N*
2...........	0.3341	0.2669	0.2665	0.09 *N*

To test the method further, copper was deposited from pure copper sulfate. This was dissolved in nitric acid and the acid was expelled by evaporation with an excess of perchloric acid, using the platinum dish in which the metal was deposited. The metal was then redeposited, washed, dried and weighed. This process was repeated three times with the same portion of copper, and the weights were 0.1559, 0.1560, 0.1557.

Silver.

The silver used was from a quantity prepared many years ago, and whose high degree of purity has been many times proved. In its preparation the chloride was reduced, and the finely divided silver was fused into large masses and electrolyzed in nitric acid solution. The electrolytic silver was fused into buttons on charcoal made from sugar.

Buttons of this silver of suitable sizes were dissolved in nitric acid and the excess of acid was driven off on the water bath. Water and an excess of perchloric acid were added and the water was evaporated. The evaporation was repeated twice. Experiments already described indicate that there remained only a trace of nitric acid, too small to influence the results. The perchlorate was dissolved in 150 cc. of water, and the solution was subjected to electrolysis with a voltage of 3 and current strength 0.2. The revolving electrode was used, but as silver oxide accumulated in considerable amount the rate of the anode was lowered and in some cases stopped for a time to prevent the throwing off of this oxide. In experiment 3 the temperature was kept at 60° during the electrolysis, to hasten the solution of the oxide. In all cases it was completely dissolved from the anode long before the current was stopped. In each case the current was continued till after the acid solution had been siphoned off and replaced by water. The following are the data:

	Silver taken.	Silver found.	Acidity.
1...........	0.1836	0.1836	0.1 *N*
2...........	0.2112	0.2112	0.06 *N*
3...........	0.1637	0.1636	0.4 *N*

Cadmium.

The cadmium used was in the form of oxide, made by Merck. It contained water, but tests failed to disclose any other impurities save a trace of lead. It was heated for an hour in a porcelain boat in a tube through which oxygen was passed. Portions were weighed in the dish to be used in the electrolysis and dissolved in a small excess of perchloric acid. The solution was made up to 150 cc. The current was started at 3.5 volts and 0.3 ampere per square decimeter of cathode surface. Later it was increased to about 0.5 ampere. The time was three hours. The cadmium formed a fairly compact layer save near the center of the dish where the anode was nearer the dish and where the movement of the solution was smaller. Like the silver, it was sufficiently adherent at all points to avoid danger of loss in washing. Three experiments gave the following values:

	Cadmium oxide.	Cadmium calculated.	Cadmium found.	Acidity.
1...........	0.3332	0.2917	0.2896	0.08 *N*
2...........	0.2131	0.1865	0.1857	0.03 *N*
3...........	0.2630	0.2302	0.2291	0.033 *N*

Of course little could be claimed for the purity of the cadmium oxide used, and its cadmium content was, therefore, determined by two of the older methods. In Experiment 4 the oxide was dissolved in a small excess of sulfuric acid and three grams of pure sodium acetate were added. In Experiment 5 the oxide was dissolved in pure perchloric acid and three grams of pure potassium cyanide were added. This gave a better deposit than those obtained in the other experiments with cadmium. In all cases there seems to be a trace of cadmium remaining in solution, as shown by a slight yellow color rather than a distinctly visible precipitate when the solutions after electrolysis are treated with hydrogen sulfide.

	Cadmium oxide.	Cadmium calculated.	Cadmium found.
4............	0.2937	0.2571	0.2537
5............	0.2716	0.2378	0.2356

As may be seen, the cadmium found in these two experiments is on the average about 1.5 milligrams smaller than that found in Experiments 1, 2 and 3. The source of this difference is as yet not clear, but it seems very probable that cadmium may be as completely separated electrolytically from dilute perchloric acid as from any other solvent.

Work is in progress on the practicability of using perchloric acid in depositing other metals.

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