The density of this sample, presumably a nearly pure isotope, is thus 11.273, distinctly less than 11.289, the density of the Australian radio-lead, and still less than the density 11.337 found for ordinary lead. The decrease is almost exactly proportional to the decrease of the atomic weight in these samples, for the atomic weight of the Australian lead was about 206.35, and that of this sample 206.085. Thus the atomic volume of the isotope ((206.08)/(11.273) = 18.281), is almost identical with that of pure lead, as indicated by our previous experiments. 18.281 is essentially equal, within the limit of error of experiment, to the value 18.277, found for ordinary lead, and to the value 18.279, found for Australian radio-lead. It is interesting to note that Australian radio-lead would be essentially duplicated as to these properties by a mixture consisting of three parts of pure isotope to one of ordinary lead.

Summary.

This brief paper describes the determination of the density of lead from Norwegian cleveite kindly furnished by Professor Gleditsch. This lead, presumably a pure isotope, was found to have a density (11.273) decidedly lower than the mixture previously studied. The corresponding atomic volume of the pure isotope is essentially equal to that of ordinary lead, as indicated by the earlier results on radio-lead from Australia.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS.]

AN ELECTRO-ANALYTICAL METHOD FOR THE DETERMINATION AND SEPARATION OF THE METALS OF THE COPPER-TIN GROUP.[1]

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Partly in collaboration with THOMAS E. PHIPPS.[2]

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Solutions containing chlorides have been considered unsuitable for the electro-analytical deposition of metals, probably on account of the oxidizing action of the liberated chlorine. Since the formation of chlorine can be prevented by the addition of reducing agents, and since such solutions present all the advantages of *simple acid electrolytes* while they are more serviceable than either the "sulfuric acid" or the "nitric acid" electrolytes advocated by Foerster[3] and by Sand,[4] respectively, it was decided to investigate their use with the more common metals, particularly with

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[1] This work was carried out at the University of Texas under the direction of Professor Schoch and presented to the University of Chicago by Mr. Brown as part of the dissertation in partial fulfillment of the requirements for the Ph.D. degree.

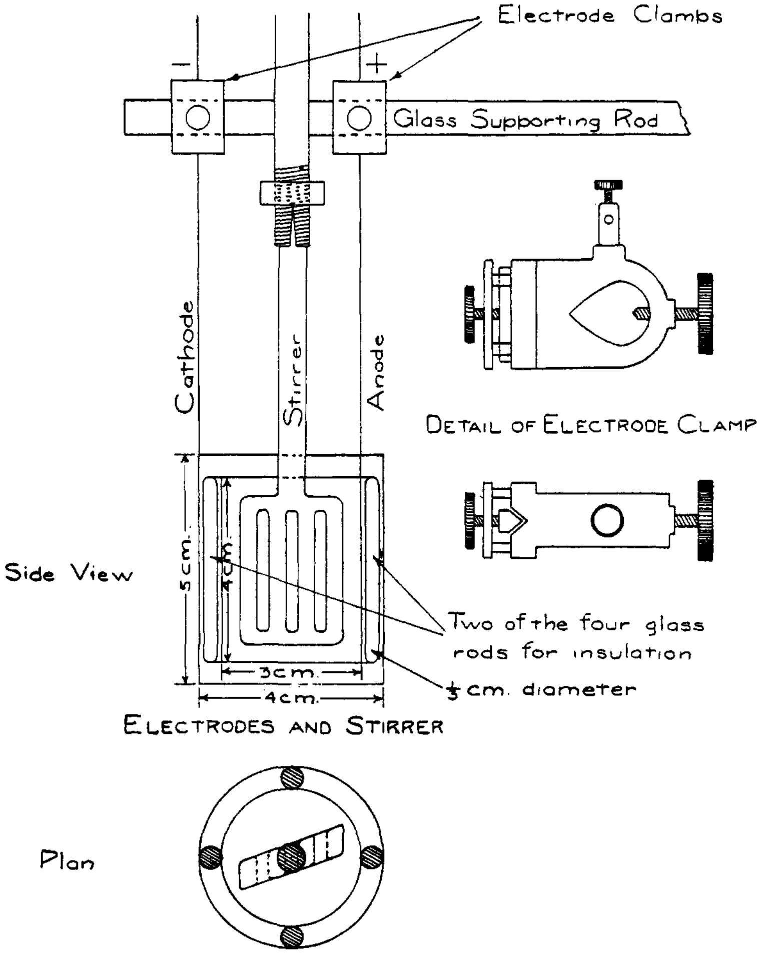
[2] Mr. Thomas E. Phipps worked out the methods given in Arts. 13, 14, 15, and 16.

[3] *Electrochemie Wässeriger Loesungen*, 23; *Z. angew. Chem.*, 19, 1842 (1906).

[4] *J. Chem. Soc.*, 91, 401 (1907).

bismuth, antimony, and tin. For antimony and tin the only method known heretofore which uses an acid electrolyte is that devised by Sand[1] and it requires the use of fairly concentrated sulfuric acid (sp. gr. 1.4), a temperature above 100°, and is altogether not as practicable or convenient a method as may be desired.

We have found that antimony, bismuth, copper, lead, tin and cadmium may be deposited quantitatively and in good form from "hydrochloric acid" electrolytes if suitable reducing agents are present in the solutions and oxides of nitrogen or nitric acid are absolutely absent; and that these electrolytes admit of the separation of all these metals from each other and from such other metals of the copper-tin group as would, if present, have to be considered.



Detail of Electrode Clamp

Electrodes and Stirrer

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[1] *J. Chem. Soc.*, 93, 1573 (1908).

Apparatus and Manipulations.

The Electrolytic Apparatus.—In all of our work we used the Sand-Fischer apparatus and electrodes.[1]

The figure on p. 1661 presents the apparatus in detail. The introduction of a clamp of a special design made it possible to remove and replace quickly either of the two concentric electrodes without disturbing the other. This method of clamping eliminated the very undesirable glass tube formerly used for insulating the stem of the cathode, holds the electrodes more rigidly, and renders it possible to keep the electrodes suspended above the bottom of the beaker, thus permitting of more efficient stirring than is possible with the electrodes resting on the bottom. The electrodes were made of a fine platinum wire gauze—about 25 meshes to the cm. with a wire 0.1 mm. in diameter. The total surface of the cathode (or outer gauze cylinder) was estimated to be about 90 sq. cm. Hence the absolute values of the currents used are also very nearly the values of the current densities per 100 sq. cm. The most suitable beaker for the electrolyzing vessel was found to be a very tall or narrow beaker of 350 cc. capacity (height, $12^1/_2$ cm.). With this beaker, the volume of electrolyte necessary to cover the electrodes is about 150 cc. The platinum anodes or cathodes were constantly reweighed during the progress of this work, and none of them decreased in weight during the operations mentioned in this paper.

The normal calomel electrode was employed as the auxiliary electrode in all of our determinations.

Special Remarks on Manipulation.—In the determination of metals that form alloys with platinum, *e. g.*, tin, lead and antimony, the platinum cathode was always covered with a deposit of copper before depositing the metal.[2]

Energetic stirring is essential to the success of these electro-analytical operations. Our stirrer made 800 revolutions per minute, but our apparatus was so rigid and the beaker so high that no loss through splashing was experienced. The sides of the beaker and the stirrer were always washed with a stream of water a short while before the end of a determination.

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[1] For a general description of the apparatus and methods of determination by "graded potential" see texts on electroanalysis, *e. g.*, Smith, *Electroanalysis*, 274–84; Classen (translated by Hall), *Quantitative Analysis by Electrolysis*, Part I; Fisher, *Electroanalytische Schnellmethoden*. The apparatus we used was made by F. Koehler, Leipzig, Germany.

[2] If the deposit of copper is too thin, these metals pass through and unite with the platinum electrode. In such cases the general treatment for the removal of metal deposits will fail to remove all of the deposit. A remnant of antimony could be removed by heating the electrode to whiteness without loss of weight to the platinum electrode, but tin and lead cannot be removed by this method.

It was observed that all of our metal deposits, when covered by a film of the electrolyte, oxidize quickly on exposure to the air. Hence a special effort was made to remove the electrolyte quickly and effectively from the cathode. If the electrolyte was to be employed for the determination of a second metal, the deposit was washed with a stream of water while the beaker was lowered away from the electrodes. If no other quantitative determination was to be made, a beaker of distilled water was quickly substituted for the electrolyte. The deposit was then washed successively in alcohol and in ether and finally dried by holding it high above a Bunsen burner flame.

All metal deposits, except those of antimony and tin, can be removed by means of nitric acid, but antimony and tin form oxides which adhere so tenaciously to the electrodes that they require the use of a brush to remove them. Hence these metals were removed electrolytically by connecting the electrode with the deposit as an anode in dilute hydrochloric acid. Antimony can also be removed by means of a mixture of nitric and tartaric acids. Lead peroxide is removed by means of a mixture of nitric and oxalic acids.

All metal deposits can be removed by immersing them in a mixture of concentrated hydrochloric acid and water (1 : 1), adding nitric acid—a few drops at a time—and proceeding as directed below under "Preparation of Electrolyte." This method of redissolving metal deposits was employed particularly for dissolving mixtures which required further separation.

Preparation of Electrolyte.—As the determination of very small amounts of any metal to be deposited is in reality the same as the determination of the last portions of larger amounts, no special determinations were made with minute quantities of metals, and the samples were all chosen so as to contain, of the metals to be deposited, the largest amounts suitable for these determinations. Whenever other metals than those to be deposited were added, they were also added in the largest proportion in which they are ever likely to be present in a practical analysis, because the probability that the deposited metal may be contaminated by other metals becomes greater as the amounts of such other metals in the electrolyte becomes greater.

The purity of the substances used for samples was always ascertained by the usual qualitative tests, in addition to the careful observation of the quantitative results attained. When pure metals were not obtainable for samples, they were either prepared electrolytically—as in the case of bismuth—or some pure definite compound of the metal was used, *e. g.*, antimony oxide, recrystallized arsenious oxide, etc.

We weighed out as much of the sample as would give a deposit of at least a tenth of a gram of any constituent, but would not give a total for any single deposit greater than two-thirds of a gram. To this we added 8–12 cc. of concentrated hydrochloric acid (sp. gr. 1.20) and an equal amount of water. Samples consisting of tin or of more reactive metals were placed in contact with platinum, under which conditions they dissolve rapidly, but if lead or metals more noble than lead were present, we added a few drops of nitric acid, not sufficient to react with the whole sample, and warmed the mixture slightly—not above 75°—in order to prevent the loss of volatile chlorides. Since it is very essential that the mixture is not overheated—even momentarily—we placed the beaker in a water bath kept at about 70° or we placed it inside of a larger beaker containing some water warmed to 70°. When the reaction ceased, we added more nitric acid, a drop at a time, and allowed each portion to react completely before adding the next one; this we continued until the whole sample had been attacked with the least possible amount of nitric acid. An excess of nitric acid is to be avoided because it will prevent the complete deposition of the metals, and can not be removed completely even by the addition of such active reducing agents as hydrazine or hydroxylamine hydrochloride. Its removal by evaporation is generally not practicable because the chlorides of several metals of this group are volatile, *e. g.*, the chlorides of arsenic, antimony and tin.

Next we added 2 g. of hydroxylamine hydrochloride (to remove the oxides of nitrogen and the free chlorine), and heated the mixture as before, not to exceed 70°. The mixture was then diluted to 150–200 cc. to suit the size of the electrolytic vessel, and electrolyzed according to the methods presented below. Some of the experimental work was done with solutions prepared in ways different from the above. Special mention will be made of this fact wherever that was the case.

The Systematic Separation of the Metals of the Copper-Tin Group.

The ultimate object of this investigation is the devising of a system for the electro-analytical separation and determination of all the common metals. The work in this paper together with some well-known analytical facts has practically enabled us to attain this object; and since the data to be presented in this paper owe a large part of their value to the fact that they fit into such a scheme, we have decided to present an outline of such a scheme here. The outline will show the relation of the different experimental results to each other and to the whole.

If arsenic is present, the sample should be dissolved as outlined above, somewhat more hydroxylamine hydrochloride (a total of 3 g.) should be added, the concentrated mixture should be transferred to a 200 cc. distilling flask (with the aid of concentrated hydrochloric acid to "wash" the remnants into the flask, or better, the whole previous treatment is made in this flask), and the arsenious chloride is distilled while a current of hydrogen chloride gas is passed through the distilling flask (Fischer's method).[1] The distillation should be continued until the residue in the distilling flask has a volume of 10 to 20 cc. It should be mentioned here that if antimony is present, a small amount of antimonous chloride may distil over, and will be determined together with arsenic if the latter is determined by titration with iodine; but this trace of antimony can be conveniently separated from the arsenic by Bunsen's method[2] and determined, or added to the residue left after distillation.

If the residue left in the distilling flask is less than the original volume (20 to 25 cc.), it should be brought up to this volume by the addition of a mixture of equal parts of water and concentrated hydrochloric acid.

The residue from the arsenic distillation is rinsed into an electrolysis beaker, and is then diluted as necessary for electrolysis. Of course, if arsenic is not present, the original concentrated solution is thus diluted. If a precipitate of mercurous chloride, of silver chloride, of gold or of platinum is present, the concentrated mixture should be diluted only partially, filtered, the precipitate washed, and the filtrate plus the washings diluted further until the solution has the volume necessary for electrolysis (150–200 cc.).

If the precipitate on the filter paper contains silver chloride, it should be treated with ammonia. Silver may be deposited quantitatively out of this solution in ammonia by a method elaborated recently in this laboratory, and presented under a separate heading at the end of this paper.

Any mercurous chloride, gold or platinum remaining on the filter may be separated and determined by well-known methods.

From the solution obtained as above described, the first metals to be deposited with the least electromotive force, will be bismuth, copper or antimony. These three metals are deposited under practically the same conditions; hence, if more than one of them is present in the electrolyte, they will be deposited together according to the directions given in Sections 13, 12, 11, 6, 5, 4, 3 or 2. The first section here mentioned presents the general method in its final form, usable with all metals present, while the other sections present the general method in the earlier form, or methods usable when only certain metals are present. These metals may be separated by methods given in Sections 16, 15, 14 or 10.

After the removal of the above metals, the next metals to be deposited from the electrolyte are tin and lead. These metals are deposited under practically the same conditions; hence will be deposited together if both

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[1] This procedure was tested quantitatively in this laboratory by Mr. R. M. King. The apparatus and procedure employed is essentially identical with that recently published in *J. Ind. Eng. Chem.*, 8, 329 (1916), except that we passed a current of hydrochloric acid gas through the apparatus, while the directions in this reference call for the addition of concentrated hydrochloric acid. The latter probably makes the operation more convenient.

[2] See Classen, *Quantitative Analysis* (translated by Harriman) ed. 1902, p. 89.

are present in the electrolyte. For details see Sections 9, 7 or 1. This alloy is readily separated by the method in Section 8.

Cadmium is the last metal in this list to be deposited from the electrolyte after the removal of the metals above. No metals "more zincic" than cadmium are considered in this outline. The term "more zincic" is employed, in preference to "more negative," to signify that the element is more active as a metal, or has a greater tendency to form positive ions —"more like zinc."

Since the relations of the facts presented in this paper are shown by the outline, it is unnecessary to indicate them again; hence we will present our results in the order in which they were obtained rather than in the order which would conform to the outline. A list of the different determinations—or section headings—is given here for convenient reference.

1. The Determination of Tin:
    (*a*) General Method.
    (*b*) A Modification of Classen's Oxalate Method.
2. The Determination of Copper.
3. The Separation of Copper from Tin.
4. The Determination of Bismuth.
5. The Determination of Antimony.
6. The Separation of Antimony (or Bismuth) from Tin.
7. The Determination of Lead.
8. The Simultaneous Deposition of Lead and Tin and their Separation.
9. The Separation of Tin from Cadmium.
10. The Separation of Copper from Antimony.
11. The Simultaneous Deposition of Copper and Antimony out of an Electrolyte Containing Copper, Antimony and Lead, and the Separation of Copper from Antimony by means of Nitric-Tartaric Acid Electrolytes.
12. The Simultaneous Deposition of Copper, Bismuth and Antimony out of an Electrolyte Containing these Metals and Tin: General Method.
13. The Simultaneous Deposition of Copper, Bismuth and Antimony out of an Electrolyte Containing These Metals and Also Tin and Lead.
14. The Separation of Bismuth from Antimony.
15. The Simultaneous Deposition of Copper and Bismuth from a Solution Containing these Metals and Antimony.
16. The Separation of Bismuth from Copper by Precipitation of the Former as Bismuth Phosphate.

1. (*a*) The Determination of Tin: General Method.—Copper plated cathodes were used for all depositions of tin.

Preliminary experiments showed that in the absence of reducing agents the greater part of the tin present in a solution of stannous chloride acidified with hydrochloric acid can be deposited rapidly in excellent form, but that the remnant could not be deposited even when the current was increased or continued for a long time. In fact, the tin finally dissolved more rapidly than it was deposited, until all the tin was redissolved. This was undoubtedly due to the high concentration of chlorine in the solution after long electrolysis, because when a suitable reducing agent is present in the electrolyte, the tin is deposited quantitatively. These trials indicate that chlorine is the main cause why many metals cannot be deposited completely from chloride electrolytes.

In the following determinations "Analyzed" pure tin was dissolved cold, in approximately 10 cc. of hydrochloric acid, sp. gr. 1.20, in contact with metallic platinum. After the addition of the reducing agent, the resulting solution was diluted to approximately 200 cc. and electrolyzed.

The maximum current density, with which a good deposit of tin may be obtained out of the "hydrochloric acid" electrolyte, *decreases* as the concentration of the tin salt *increases*. With amounts of tin as high as 0.7 g. in 200 cc., a current of 1.5 amperes gave, with the electrodes employed, a good deposit at temperatures ranging from 30 to 70°. With higher current densities, the relatively concentrated solutions gave granular deposits, and even "trees," but less concentrated solutions gave good deposits even with somewhat higher current densities. Since 0.7 g. would be as large an amount of tin as would be used ordinarily for analysis, and as 1.5 amperes may be safely used with this concentration of 0.7 g. in 200 cc., this amount of current was used at the start in all the determinations of tin.

The "end point" was determined by ascertaining whether or not an increase in the weight of the deposit was obtained upon replacing the electrode in the electrolyte, and electrolyzing further. The result was also confirmed by qualitative tests.

TABLE I.

Reducing agent.		Time.	Tin.		
Substance.	Grams.	Minutes.	Present.	Found.	Error. %.
$NH_2OH.HCl$	4	95	0.4370	0.4380	+0.23
		90	0.2460	0.2466	+0.24
		90	0.6972	0.6970	+0.03
		120	0.3046	0.3052	+0.20
		120	0.3000	0.3000	0.00
$(COOH)_2.2H_2O$	10	75	0.3580	0.3572	—0.24
		75	0.3830	0.3822	—0.22
		85	0.2070	0.2064	—0.29

A comparison of the results obtained with these and other reducing agents is of special interest. With hydroxylamine hydrochloride, tin is deposited completely and in a comparatively short period of time. With oxalic acid, a trace of tin always remains in the electrolyte, that is, the tin is deposited almost, but not quite, completely. With formaldehyde the deposition is decidedly incomplete, though more extensive than would be the case if no reducing agent were employed. The fact that with formaldehyde the deposition is incomplete is rather surprising because, in some respects, formaldehyde is a stronger reducing agent than hydroxylamine; but this anomaly may be due to the fact that formaldehyde acts as an oxidizing agent towards energetic reducing agents; hence perhaps toward stannous chloride.

1. (*b*) A Modification of Classen's Ammonium Oxalate Methods for the Determination of Tin.—It is well known that tin may be completely deposited out of a solution to which both ammonium oxalate and oxalic acid have been added. However, the oxalate methods heretofore employed have some undesirable features: the procedure recommended by Classen[1] gives an excellent deposit, but requires a long period of time (nine hours); while Exner's[2] rapid method requires the use of a "hot saturated" solution of ammonium oxalate, which is somewhat troublesome to handle, and the deposit is loosely adherent and powdery. Hence an improvement of the "oxalate method" is desirable. Since we found that the maximum current density with which a good deposit may be obtained from Classen's oxalate electrolyte increases as the concentration of the tin decreases, we concluded to combine this fact with the fact stated at the beginning of the determination of tin, namely, that even in the absence of a reducing agent tin may be deposited almost completely from a chloride electrolyte. The new "oxalate method" thus devised is carried out as follows: The greater part of the tin is deposited rapidly out of the simple "hydrochloric acid electrolyte to which no reducing agent has been added;" then the ammonium oxalate and oxalic acid are added and the remnant of the tin is deposited fairly rapidly. A current of 1.5 amperes may be used during the whole determination. "Time I" in the table below shows the number of minutes during which the original "hydrochloric acid" solution was electrolyzed and "Time II" the number of minutes during which the solution was electrolyzed after the ammonium oxalate and oxalic acid have been added. The modification places this "oxalate method" in the list of "rapid methods."

TABLE II.

Substance, grams.		Time, minutes.			Tin.		
$(NH_4)_2C_2O_4$.	$H_2C_2O_4.2H_2O$.	I.	II.	Total.	Present.	Found.	Error. %.
4	10	45	45	90	0.3112	0.3114	+0.06
7	10	45	45	90	0.3088	0.3092	+0.13
7	18	60	45	105	0.3157	0.3156	—0.03
7	18	60	45	105	0.3542	0.3537	—0.13
7	18	75	45	120	0.4852	0.4849	—0.06
10	18	80	55	135	0.6838	0.6834	—0.06
7	16	45	45	90	0.3550	0.3550	0.00
7	17	45	45	90	0.2674	0.2675	+0.04
4	10	45	30	75	0.2608	0.2606	—0.08

2. The Determination of Copper.—It is impossible to deposit copper in good condition from a simple solution of cupric chloride acidified with

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[1] See Classen-Hall, "Quantitative Analysis by Electrolysis," 1913, p. 136.

[2] See Smith, "Electroanalysis," 1907, p. 168.

hydrochloric acid, but in the presence of suitable reducing agents copper can be deposited quantitatively and in excellent form, provided the concentration of the copper does not exceed 0.4 g. per 100 cc.—which is from 0.6 to 0.8 g. for the usual volume employed—with greater concentrations of copper, no electrolytic deposit is obtained.

The "most zincic" cathode potential with which copper could be obtained in good form is approximately —0.60 volt against the "normal calomel electrode." This is practically the potential at which hydrogen is evolved from this electrolyte on copper; hence the appearance of hydrogen may be used to limit the applied voltage. The determinations below marked "hydrogen limit" have been made in this way, that is, by keeping the current or voltage just low enough to avoid the evolution of hydrogen. The least "zincic" cathode potential with which copper may be practically completely deposited is —0.40 volts against the calomel electrode, but frequently 0.1 to 0.3% of copper cannot be deposited at this potential and in general complete deposition is secured only with a cathode potential of —0.50 volt. This potential just barely admits of the separation of copper from tin or lead. Naturally, when the cathode potential is limited at any value between —0.50 and —0.40 volt, the deposit of copper is certain to be free from tin or lead, but a few tenths per cent. of copper may not be deposited.

Metals more "zincic" than tin or lead are kept out of the copper deposit by not allowing the cathode potential to become more zincic than —0.60 volt or by keeping the potential below that with which hydrogen begins to be evolved.

The salts of none of these "more zincic" metals, except those of iron, exert any specific effect; but iron salts prevent the deposition of copper, unless hydroxylamine hydrochloride is employed as the reducing agent.

In connection with the selection of suitable reducing agents for copper, we found that a weak reducing agent such as tartaric acid could be used for its separation from cadmium, nickel, cobalt, chromium and manganese, but that more time is required when this reducing agent is employed than when one of the more active reducing agents, such as formaldehyde or hydroxylamine hydrochloride, is employed. Hydroxylamine hydrochloride is really the only reducing agent that gave good results under all conditions; hence we have used it rather generally.

Special attention is here called to the fact that the behavior of the cathode potential during the deposition of a metal furnishes the operator a reliable automatic indication of the "end point." As the amount of the metal ion in the solution decreases and finally becomes zero, it is necessary to reduce the applied voltage so that the current finally reaches a low "residual" value, or becomes practically zero. In our work the "end points" were all ascertained in this way, which accounts for the differences in the re-

TABLE III.

Other metals present.	Reducing agent. Subst.	Volts.			Amp.		Time.	Copper.		Error. %.
		Applied.		Against HgCl electrode.						
		Max.	Min.		Max.	Min.		Present.	Found.	
....	Formalin 10 cc.	2.0	1.6	—0.40	3.0	0.05	45	0.2700	0.2698	—0.07
....		2.0	1.6	—0.40	3.0	0.05	50	0.3722	0.3720	—0.05
....		2.0	1.6	—0.40	4.0	0.05	30	0.3084	0.3080	—0.13
....		2.0	1.6	—0.40	4.0	0.05	30	0.3962	0.3960	—0.05
....	Tartaric acid 10 g.	2.0	1.5	—0.40	7.0	0.0	180	0.5194	0.5196	+0.04
....		2.3	1.3	—0.40	8.0	0.0	70	0.3292	0.3298	+0.18
....		2.1	1.5	—0.40	7.0	0.0	150	0.3785	0.3780	—0.14
....		2.1	1.5	—0.40	6.0	0.0	70	0.3642	0.3650	+0.22
Ammonia......		2.1	1.5	—0.40	7.0	0.1	130	0.4624	0.4616	—0.16
Ammonia......		2.0	1.5	—0.40	6.0	0.1	160	0.3000	0.2995	—0.17
Sodium........		2.2	1.5	—0.40	7.0	0.0	75	0.4320	0.4316	—0.09
Potassium......		1.9	1.5	—0.40	4.0	0.0	140	0.3411	0.3412	+0.03
Potassium......		1.8	1.5	—0.40	3.0	0.0	180	0.5520	0.5510	—0.19
Cadmium......		2.3	1.5	—0.40	6.0	0.0	60	0.5650	0.5640	—0.18
Nickel.........		1.0	1.5	—0.40	4.0	0.0	85	0.2535	0.2528	—0.28
Cobalt.........		2.0	1.5	—0.40	4.0	0.0	60	0.5120	0.5118	—0.04
Chromium.....		2.0	1.5	—0.40	4.0	0.1	180	0.5072	0.5070	—0.04
Chromium.....		2.1	1.5	—0.40	6.0	0.0	205	0.5618	0.5612	—0.10
Manganese.....		2.0	1.5	—0.40	4.0	0.3	190	0.4222	0.4222	±0.00
None..........	$NH_2OH.HCl$ 2 g.	2.1	1.2	—0.40	6.5	0.0	30	0.7342	0.7328	—0.18
None..........		2.8	1.4	—0.40	7.5	0.0	30	0.6136	0.6139	+0.05
None..........		2.0	1.2	—0.40	4.0	0.0	20	0.2922	0.2918	—0.13
None..........		2.0	1.2	—0.40	4.0	0.0	15	0.3552	0.3548	—0.11
None..........		2.0	1.2	—0.40	5.0	0.0	15	0.4016	0.4015	—0.03
None..........		1.6	1.5	—0.40	3.0	0.0	30	0.3485	0.3486	+0.03
Iron...........		1.6	1.3	—0.40	4.0	0.0	60	0.4624	0.4622	—0.04
None..........		2.5	1.0	—0.60	10.0	0.0	10	0.4232	0.4230	—0.04
None..........		2.4	1.65	—0.60	8.0	0.0	25	0.4094	0.4100	+0.15
None..........		2.2	1.65	—0.60	7.0	0.0	35	0.4006	0.4000	—0.15
None..........	Formalin 10 cc.	2.35	1.65	—0.60	8.0	0.2	20	0.3426	0.3426	±0.00
None..........		2.5	2.0	—0.60	10.0	0.1	45	0.6320	0.6318	—0.03
None..........		1.8	1.4	Hydr. Limit	2.0	0.05	45	0.4378	0.4374	—0.04
None..........		1.8	1.6	" "	2.0	0.05	50	0.2598	0.2598	±0.00
None..........	$NH_2OH.HCl$ 2 g.	1.6	1.2	" "	2.0	0.05	60	0.2880	0.2882	+0.06
None..........		1.5	1.5	" "	..	..	25	0.4388	0.4392	+0.09
None..........		1.5	1.5	" "	..	..	45	0.4640	0.4638	—0.04
None..........		1.5	1.5	" "	..	..	50	0.6463	0.6454	—0.15

quired lengths of time given in the table of results below. We note that the minimum lengths of time for the determination of copper were required when hydroxylamine hydrochloride was employed, which is another reason why we believe that this is the most suitable reducing agent for these determinations.

Sometimes copper will not begin to be deposited immediately when the current is turned on. This is usually due to the fact that too much nitric acid has been used in dissolving the sample. Occasionally the disturbing factors are removed by the passage of the electric current, but generally the trouble is irremediable. This is true not only for the deposition of copper but for the determination of other metals.

The solution usually becomes clear long before the copper is completely deposited; this is due to the conversion of the cupric salt to cuprous salt, and should not mislead the experimenter into believing that the copper is nearly all deposited. A qualitative test for copper should not be attempted for a long time after the blue color has disappeared, because the liquid removed for testing cannot be returned to the electrolyte.

Pure electrolytic copper was used for the determinations below. The electrolyte was prepared by the general method described above. Besides hydroxylamine hydrochloride, various other reducing agents were used with copper, as the experiments show.

3. The Separation of Copper from Tin.—Weighed amounts of copper and tin were dissolved and the electrolyte was prepared according to the general directions given at the beginning of this paper. Special care was taken to avoid an excess of nitric acid, and to avoid heating the solution above 75°, or it was found impossible to recover all of the dissolved metals.

The copper was deposited by limiting the cathode potential to —0.40 volt against the "normal calomel electrode." The cathode was weighed, replaced in the solution, two grams additional of hydroxylamine hydrochloride were added, and the tin was deposited in accordance with the directions given for depositing tin. The following results were obtained:

TABLE IV.

Copper.			Tin.		
Present.	Found.	Error. %.	Present.	Found.	Error. %.
0.5165	0.5165	0.00	0.6126	0.6147	+0.34
0.4502	0.4482	—0.42	0.3148	0.3162	+0.42
0.3334	0.3344	+0.30	0.2124	0.2120	—0.20
0.5002	0.5004	+0.04	0.5002	0.5008	+0.12
0.5002	0.5006	+0.08	0.5860	0.5858	—0.03

Some of our students secured excellent results when they limited the cathode potential to —0.50 volt. (See also Section 2, second paragraph.) Qualitative tests were made to determine whether the separation was complete. The absence of tin in the copper deposit was shown by the absence of a precipitate of stannic oxide when the copper deposit was dissolved in nitric acid. The absence of copper in the "residual" electrolyte was shown by the "ferrocyanide test." Finally, after the deposition of the tin, the solutions were treated with hydrogen sulfide to ascertain whether all the tin had been deposited; no discoloration of the solution was produced by the hydrogen sulfide.

4. The Determination of Bismuth.—In order to obtain a good deposit of bismuth out of an electrolyte which contained hydrochloric acid and hydroxylamine hydrochloride, it was necesesary to limit the potential of the cathode against the "normal calomel electrode" to —0.25 volt, or less, until most of the metal had been deposited and the current had been reduced to a very small fairly constant value. Then the applied voltage was raised gradually so that the residual current was not appreciably increased, and the electrolysis continued until the potential of the cathode against the calomel electrode attained the value —0.5 volt. Then the current was interrupted.

"Analyzed" pure oxychloride of bismuth was employed for the following determinations. The samples were dissolved in 5 cc. hydrochloric acid, sp. gr. 1.2, and 2 g. of hydroxylamine hydrochloride were then added. The solution was diluted to 200 cc., heated to 55–75° and subjected to electrolysis in the manner stated before.

TABLE V.

	Bismuth.		
BiOCl.	Present.	Found.	Error. %.
0.4938	0.3958	0.3954	—0.10
0.4049	0.3245	0.3247	+0.06
0.3930	0.3150	0.3150	—0.00
0.4298	0.3445	0.3442	—0.09
0.4551	0.3648	0.3646	—0.06

5. The Determination of Antimony.—Several peculiar properties of antimony and its salts must be considered in connection with its electrolytic determination. If hydrogen is evolved during the electrodeposition of the metal, some of the latter will escape in the form of stibine. If the electrodeposition takes place below 50°, the impure "explosive" antimony is deposited;[1] while above 70° the tendency of the antimony chloride solutions to hydrolyze increases rapidly with increase of temperature, and antimony chloride will be lost by volatilization. Our electrolytic method was designed to avoid all these sources of error.

Weighed samples of antimonous oxide, Sb_2O_3, "Analyzed" were treated with 20 cc. of hydrochloric acid, sp. gr. 1.20 (more than is used for other metals—on account of the hydrolyzing tendency of the antimony), and with 2 g. of hydroxylamine hydrochloride. The resulting solution was

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[1] *Z. physik. Chem.*, **52**, 129 (1905).

diluted to 200 cc. The dilution of any solution containing antimony chloride must always be made very quickly while stirring, in order to prevent hydrolysis. The electrolyte was heated to a temperature between 50 and 75° and deposited on copper-plated electrodes with a cathode potential of —0.30 to —0.40 volt against the normal calomel electrode until the current dropped to "zero." The following results were obtained

TABLE VI.

Time.	Sb_2O_3.	Antimony. Present.	Antimony. Found.	Error. %.
15 min	0.6990	0.5825	0.5814	—0.20
10 min	0.4390	0.3658	0.3647	—0.30
10 min	0.5542	0.4618	0.4600	—0.40
8 min	0.2456	0.2047	0.2048	+0.05
15 min	0.4708	0.3923	0.3928	+0.12
5 min	0.4844	0.4038	0.4044	+0.15

6. The Separation of Antimony (or Bismuth) from Tin.—The sample was prepared as previously stated, except that 15 cc. of concentrated hydrochloric acid were employed (to prevent the hydrolysis of the antimony salts), and 4 g. hydroxylamine hydrochloride were added. The solution was diluted to 200 cc., heated to 50°, and electrolyzed with the cathode potential at —0.40 volt until the current reached a constant minimum which indicated that the deposition of the antimony was complete.

TABLE VII.

Antimony. Present.	Antimony. Found.	Error. %.	Tin. Present.	Tin. Found.	Error. %.
0.2107	0.2106	—0.05	0.2878	0.2886	+0.29
0.3443	0.3448	+0.14	0.3044	0.3032	—0.40
0.2757	0.2760	+0.11	0.5582	0.5562	—0.35
0.2580	0.2582	+0.08	0.3482	0.3484	+0.06
0.3180	0.3182	+0.06	0.3712	0.3706	—0.16
0.4457	0.4444	—0.29	0.4948	0.4926	—0.44
0.2105	0.2006	+0.05	0.2846	0.2838	—0.29
0.3945	0.3946	+0.03	0.6578	0.6580	+0.03

This is evidently to be preferred to the tedious gravimetric separation of these two metals.

Since bismuth may be deposited out of the same electrolytes at a potential slightly "less zincic" than that required for antimony, the separation of bismuth from tin can undoubtedly be effected under the same general conditions given for the determination of bismuth. As much of this metal as possible must be deposited while the cathode potential is limited to —0.25 volt, or less, against the calomel electrode; then the applied voltage is to be raised, without increasing the residual current, until the cathode potential has attained the value —0.40 volt.

7. The Determination of Lead.—Copper-plated electrodes were used for all lead deposits.

Weighed quantities of "Analyzed" lead chloride were dissolved in 200 cc. of hot water to which 10 cc. of concentrated hydrochloric acid had been added. The reducing agent was added and the solution electrolyzed while warm (60–70°) with a current of 1.5 amperes for 25 or 40 minutes. The "end point" was determined as with tin—by replacing the weighed electrode in the electrolyte, electrolyzing further, and weighing the electrode again. The solution was also treated with hydrogen sulfide to prove the absence of lead. The following results were obtained:

TABLE VIII.

Reducing agent employed.	Amount of lead chloride.	Lead. Present.	Lead. Found.	Error. %
Oxalic acid	0.5912	0.4403	0.4396	−0.16
Oxalic acid	0.7292	0.5432	0.5430	−0.04
Hydroxylamine hydrochloride	0.8970	0.6681	0.6674	−0.10
	0.3292	0.2452	0.2456	+0.16
	0.3462	0.2579	0.2580	+0.04
	0.3746	0.2792	0.2790	−0.07
Formalin	0.2734	0.2036	0.2038	+0.10
	0.3282	0.2444	0.2438	+0.16
	0.3042	0.2265	0.2262	−0.13
	0.3036	0.2260	0.2258	−0.09

These results are more reliable than those obtained by depositing lead as a peroxide.[1] One remarkable feature of this deposition of lead is that formaldehyde may be employed while it cannot be employed in the deposition of tin. The difference may be due to the fact that the lead chloride, unlike stannous chloride, is not an active reducing agent.

8. The Simultaneous Deposition of Lead and Tin and Their Separation. —The potentials at which tin and lead are deposited from acidified chloride solutions are so close together that an electrolytic separation is impossible. On this account, and because these metals alloy readily, they are deposited together under the same conditions under which either one is deposited; hence both together may be separated from other metals just as either one alone may be deposited. This leaves us merely the special problem of their separation.

When an alloy of tin and lead is treated with nitric acid, the insoluble stannic oxide adsorbs some of the lead salt; hence the separation is incomplete. It occurred to us that it might be possible to find a salt which would be adsorbed more readily than the lead nitrate, and which, if added to the mixture, would allow the lead salt to be released. When potassium nitrate is added to the nitric acid a complete separation of tin and lead is effected. The lead may be deposited as peroxide from one of the two separate portions thus obtained; and the tin may either be obtained by difference, or it may be determined by treating the insoluble stannic

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[1] Sand, *Faraday Society*, 5, 210.

oxide with concentrated hydrochloric acid and hydroxylamine hydrochloride, and depositing the tin by electrolysis.

This separation was carried out according to two slightly different methods of procedure. In the first, the mixture of tin and lead was treated with nitric acid in the usual manner, the mixture was heated until all nitrous oxide fumes were expelled, diluted to 200 cc., boiled, stirred for ten minutes with the stirrer of the electrolytic apparatus and filtered. The impure precipitate was washed back into the beaker, 10 g. potassium nitrate were added, the mixture was boiled, stirred and filtered as above. The lead in the filtrate was determined by electrodeposition on the anode as lead dioxide. The stannic oxide was immediately treated with concentrated hydrochloric acid in presence of hydroxylamine hydrochloride, and the tin deposited from the resulting solution by our method.

TABLE IX.

Lead.				Tin.		
Present.	PbO_2.	Found.	Error. %.	Present.	Found.	Error. %.
0.3886	0.4474	0.3874	−0.31	0.6644	0.6636	−0.12
0.5050	0.5828	0.5047	−0.06	0.7850	0.7846	−0.05
0.5546	0.6394	0.5537	−0.16	0.3452	0.3452	0.00

In the second method, the mixture of tin and lead was dissolved in 10 cc. of concentrated nitric acid in the presence of 10 g. of potassium nitrate dissolved in 40 cc. of water. The mixture was heated as before to expel the nitric oxide fumes, diluted to 200 cc., boiled, stirred for fifteen minutes with the stirring apparatus used for the deposition, cooled, filtered and washed. The tin and the lead were then determined as stated above.

TABLE X.

Lead.				Tin.		
Present.	PbO_2.	Found.	Error. %.	Present.	Found.	Error. %.
0.4718	0.5462	0.4730	+0.25	0.4310	0.4310	0.00
0.4074	0.4710	0.4079	+0.12	0.4414	0.4422	+0.18
0.3052	0.3520	0.3048	−0.13	0.5126	0.5130	+0.08

In addition to the above quantitative separation, a qualitative test was made to show that none of the lead salt remained in the stannic oxide. The precipitate was dissolved in a mixture of concentrated hydrochloric acid and hydroxylamine hydrochloride, then diluted and treated with hydrogen sulfide, and the precipitate treated with yellow ammonium sulfide; it dissolved completely.

9. The Separation of Tin from Cadmium.—Mixtures containing known amounts of stannous and cadmium chlorides were prepared by measuring out portions of solutions of known concentrations of these salts. Sufficient hydrochloric acid was added to prevent hydrolysis, 2 g. of hydroxylamine hydrochloride were added, and the requisite amount of water to bring the volume to 200 cc. With the solution warmed to 70°, the tin was deposited by limiting the current to 1.5 amperes until the cathode potential had attained the value —0.70 volt against the "normal calomel electrode." Then the current was reduced in order to keep the cathode potential constant until the current attained a constant "residual" value. The tin was found to have been completely deposited. After weighing, the cathode was replaced, the applied electromotive force was raised until a current of one ampere passed (higher currents gave spongy deposits of cadmium), and this current was continued until a qualitative test showed the absence of cadmium. About forty to sixty minutes were required to complete the deposition of the cadmium.

TABLE XI.

Tin.			Cadmium.		
Present.	Found.	Error. %.	Present.	Found.	Error. %.
0.4710	0.4710	0.00	0.3010	0.3010	0.00
0.4710	0.4712	+0.05	0.3010	0.2994	—0.50
0.4710	0.4710	0.00	0.3040	0.3048	+0.26
0.4710	0.4700	—0.22	0.3010	0.3006	—0.13

No trial was made to separate lead, or lead and tin, from cadmium, but from our point of view no reason can be seen why the separation could not be accomplished in the same way as the separation of tin from cadmium.

10. The Separation of Copper from Antimony by Means of Hydrochloric-Tartaric Acid Electrolytes.—Copper and antimony were dissolved as usual in hydrochloric acid with the minimum amount of nitric acid. Then 8–10 g. of tartaric acid were added, the mixture was diluted and electrolyzed. The electrolyte was kept cool, not to exceed 25°, because at higher temperatures greater potentials are required to deposit the copper completely out of acidified tartrate electrolytes, and the separation of copper from antimony becomes impossible. A current of two amperes was allowed to pass until the "observed cathode potential" had attained the value —0.50 volt; then the current was reduced so as to keep the "cathode potential" constant at —0.50; when the current had become practically zero, the applied voltage was kept constant until the cathode potential rose to —0.65 volt; then the experiment was terminated. Of course, this separation can be made with lower potentials, but not as rapidly.

Copper.			Copper.		
Present.	Found.	Error. %.	Present.	Found.	Error. %.
0.3596	0.3604	+0.22	0.3444	0.3442	—0.06
0.4424	0.4432	+0.18	0.4582	0.4588	+0.13
0.4782	0.4778	—0.08	0.5790	0.5788	—0.03

As the deposit was excellent in color and the remaining electrolyte gave no indication of copper with the ferrocyanide test, the separation was considered to be quantitative. No reliable method is known for depositing the antimony out of tartrate solution; we found that only a portion of the antimony could be deposited.

11. The Separation of Copper and Antimony from Lead by the General Method and the Separation of Copper from Antimony by means of Nitric-Tartaric Acid Electrolytes.—In this procedure we separated copper and antimony from lead by depositing the first-mentioned two metals together. We did not make the corresponding separation of copper and antimony together from tin because the similarity in the properties of these metals indicates that this separation can be carried out by the method given under this heading—an idea that is confirmed by the results given in Section 13.

Weighed quantities of copper, antimony and lead were dissolved in the usual manner, except that 20 cc. of concentrated hydrochloric acid were used in place of 10 cc. to prevent hydrolysis of the antimony salts. To this mixture, 2 g. hydrazine hydrochloride were added, the mixture was diluted slightly and heated slowly to 60° with constant stirring. There was an evolution of gas, which was probably due to the action of the hydrazine on the nitrous oxides. Then the solution was diluted while hot, to 200 cc. and electrolyzed with a copper plated cathode. The copper and antimony were deposited together by limiting the cathode potential to —0.40 volt against the normal calomel electrode until the current fell to a tenth of an ampere; then the applied voltage was kept constant until the cathode potential against the auxiliary electrode was —0.50. The electrode with the deposit of copper and antimony was weighed and the deposit was dissolved in diluted nitric acid in the presence of 10 g. of tartaric acid. Then the copper was deposited with the cathode potential limited to —0.30 volt, and the temperature limited to 20°. The copper deposit had an excellent appearance. The weight of the antimony was obtained by subtracting the weight of the second deposit from the first. The lead, still in the first electrolyte, was deposited on a copper plated cathode.

TABLE XII.

Copper		Error.	Antimony.		Error.	Lead.		Error.
Present.	Found.	%.	Present.	Found.	%.	Present.	Found.	%.
0.5516	0.5516	0.00	0.5726	0.5730	—0.07	Not determined		
0.3040	0.3050	+0.13	0.3956	0.3948	—0.20	0.4250	0.4258	+0.18
0.4372	0.4378	+0.13	0.4684	0.4674	—0.10	0.6026	0.6012	—0.22
0.4130	0.4120	—0.12	0.4836	0.4838	+0.04	0.6034	0.6039	+0.07
0.3382	0.3382	0.00	0.3906	0.3900	—0.15	0.4762	0.4772	+0.21

12. The Simultaneous Deposition of Antimony, Bismuth and Copper out of Electrolytes Containing These Metals and Tin.—The first three were separated from tin by depositing them together according to the directions given for the determination of bismuth, Section 4.

Bi + Cu + Sb. Present.	Bi + Cu + Sb. Found.	Error. %.
1.0930	1.0922	—0.08
0.9370	0.9380	+0.11

The separation of these metals from solutions containing both lead and tin has been accomplished by the same method as that here employed (see Section 13).

In the separation of antimony, bismuth and copper from tin, it was noted that bismuth always came out first; in other words, bismuth is deposited from acid chloride solutions at a lower "cathode potential" than either copper or antimony, hence should be placed lower in the electromotive series than copper, while antimony should be placed above copper. However, the deposition potential of bismuth is so near to that of copper that it was found impossible to separate it from the latter out of these electrolytes.

13. The Simultaneous Deposition of Copper, Bismuth and Antimony out of Electrolytes Containing These and also Lead and Tin.—Samples of weighed quantities of copper, of bismuth oxychloride, and of antimony oxide, and unweighed quantities of lead and tin were dissolved according to the usual procedure. When lead chloride was present in relatively large amounts, the crystals of this substance were removed by filtration. The copper, bismuth and antimony were deposited by the method given for the determination of bismuth, except that it was found necessary to limit the cathode potential to —0.20 volt against the normal calomel electrode in order to obtain good deposits. As in the determination of bismuth, finally the cathode potential was allowed to "rise" to —0.35 volt. The results obtained were as follows:

TABLE XIII.

Cu + Sb + Bi present.	Cu + Sb + Bi found.	Error. %.	Cu + Sb + Bi present.	Cu + Sb + Bi found.	Error. %.
0.7783	0.7787	+0.05	0.7805	0.7811	+0.09
0.7587	0.7589	+0.03	0.7338	0.7344	+0.09
0.7199	0.7189	—0.14	0.7754	0.7754	+0.00
0.5194	0.5188	—0.11	0.8077	0.8085	+0.10
0.6913	0.6916	+0.04			

From 45 to 60 minutes were required for the separation.

The bismuth was apparently deposited first, and at the same time the solution lost the blue-green color of the cupric ion; then a purple grape-colored alloy of copper and antimony began to be deposited, and the cathode potential fell, it being necessary to again raise the current; finally, a grayish black deposit of apparently pure antimony covered the electrode. Sometimes it happened that there were alternate depositions of the alloy and of the antimony, but the deposition of the alloy was heralded by a "drop" in the cathode potential.

14. The Separation of Bismuth from Antimony.—Definite quantities of bismuth oxychloride and of antimony oxide were weighed out into the same electrolyzing beaker, dissolved in 5–7 cc. of hydrochloric acid (sp. gr. 1.2), and the resulting solution was diluted up to 150 or 175 cc.; 4–8 g. of potassium tartrate were added, and the solution was boiled for several minutes. Two grams of hydroxylamine hydrochloride were added, the temperature was raised to 70°, and the solution was electrolyzed with the cathode potential limited to 0.20 volt against the normal calomel electrode. Since bismuth "burns" very easily while being deposited, it was necessary to watch the cathode potential carefully and to prevent it from exceeding the limit of —0.20 volt. The main electrolyzing current was reduced continuously until there was no further tendency for the cathode potential to rise. Long before this state of affairs was attained, the electrolyzing current was practically zero—yet it was necessary to continue electrolysis and to decrease the applied voltage until the cathode potential showed no disposition to rise. This required 20–30 minutes. By this procedure, bismuth was deposited quantitatively and entirely free from any antimony. The results obtained were as follows:

	Bismuth.		
Sb_2O_3.	Present.	Found.	Error %.
0.20	0.3160	0.3150	—0.31
0.20	0.3288	0.3284	—0.12
0.30	0.3888	0.3888	±0.00
0.40	0.3451	0.3446	—0.20

The deposits were all in excellent condition.

15. The Separation of Copper and Bismuth from Antimony.—As the easiest method of removing a deposit containing antimony from the electrode is with nitric and tartaric acids, an attempt was first made to deposit copper and bismuth simultaneously from a nitric-tartaric acid electrolyte which contained these metals and antimony. A triple alloy obtained as stated in Section 13 was dissolved in the minimum amount of nitric acid and 5–6 g. of tartaric acid. The solution was diluted to 150 or 175 cc. and electrolyzed. The temperature was kept at 25° or below, as in the separation of copper from antimony in the same electrolyte (Section 11). At the beginning of the deposition, the cathode potential was about —0.10 volt against the normal calomel electrode, but toward the end it was allowed to rise to —0.20 volt. Copper was the first metal to be deposited; this order was the opposite of that observed in chloride electrolytes. The solution was not free of copper when the color of the cupric ion had disappeared, but a considerable amount of copper was still present in the cuprous state while bismuth was being deposited. It happened quite often that there were alternate depositions of bismuth and of copper long after all color had disappeared. On account of the solubility of the copper in the nitric acid, siphon washing was resorted to in most instances. Some of the results which we obtained are as follows:

TABLE XIV.

Sb present.	Cu + Bi present.	Cu + Bi found.	Error. %.
0.20	0.5368	0.5347	—0.40
0.40	0.4794	0.4814	+0.40
0.20	0.4607	0.4629	+0.45
0.30	0.5303	0.5298	—0.10
0.20	0.5005	0.5034	+0.58
0.20	0.4594	0.4608	+0.30

The end point of the determination was indistinct, and the high results show that, in the deposition of the last traces of copper, antimony in small amounts was probably deposited with it. The results were not considered satisfactory.

We next tried the separation in acidified chloride electrolytes. A triple alloy obtained as in Section 12 or 13 was dissolved from the platinum electrode as follows: 25–30 cc. of 1 : 3 hydrochloric acid were warmed up to about 60° in an electrolyzing beaker, the electrode was put in, and then a very few drops of conc. nitric acid were added, care being taken to use the least amount necessary to start a moderate attack on the alloy. When all of the sample had been dissolved, crushed ice was added sufficient to lower the temperature to 10° or below; then about 5 g. of tartaric acid were added. Electrolysis was carried out at this low temperature; at higher temperatures there appears to be an extensive formation of a complex tartrate-copper ion, from which the copper cannot be recovered. From time to time, small lumps of ice were added to the electrolyte to keep its temperature down.

The cathode potential was limited at the beginning to —0.15 or —0.20 volt against the normal calomel electrode, but to deposit the last of the copper it was allowed to rise to —0.40 volt. Hydrogen began to be evolved soon after, and the experiment was terminated. From 90 to 120 minutes was the time required for the deposition of the samples in the table below.

TABLE XV.

Sb present.	Copper and bismuth. Present.	Copper and bismuth. Found.	Error. %.
0.23	0.5552	0.5558	+0.10
0.30	0.6750	0.6748	—0.03
0.30	0.7156	0.7162	+0.08
0.20	0.6752	0.6746	—0.09

16. The Separation of Bismuth from Copper.—Bismuth cannot be separated from copper by the "graded potential" method, but either bismuth or copper can be separated from antimony. When all three metals are present, the first procedure to suggest itself is to remove either bismuth or copper from the solution, and to separate the other two by one of the methods given above. Hence we made a complete study of Moser's method[1] for precipitating bismuth phosphate in order to ascertain if bismuth could thus be removed quantitatively from solutions of these three metals.

Pure deposits of bismuth were prepared according to the directions in Section 4. The deposit was dissolved in the least possible amount of nitric acid (3–5 cc.). Tartaric acid was also used in order to reproduce the conditions which would be obtained in an actual separation of bismuth from copper and antimony. A slight excess of a 10% solution of ammonium phosphate was added to the hot solution. After a short period of digestion, the precipitate was transferred to a filter paper, and was washed with a decinormal solution of nitric acid to which a few cubic centimeters of the precipitant had been added. The bismuth was dissolved in hydrochloric acid and deposited according to the method given above for its determination. This was done first, with bismuth alone in the solution, then with copper present, and finally in the presence of antimony. The following results were obtained:

TABLE XVI.

Cu.	Sb.	Tartaric acid.	Bismuth. Present.	Bismuth. Found.	Error. %.
None	None	5 g.	0.9172	0.9140	—0.34
None	None	5 g.	0.6860	0.6859	—0.01
None	None	5 g.	0.8912	0.8912	±0.00
0.25	None	5 g.	0.5678	0.5666	—0.21
0.12	None	5 g.	0.6066	0.6042	—0.39
None	0.24	5 g.	0.6068	0.6233	+2.7
None	0.16	5 g.	0.6068	0.6200	+2.1

These results show that bismuth phosphate is precipitated quantitatively and in pure form when it is present alone in the electrolyte or together with copper, but not when it is together with antimony. On this account the order of procedure above suggested had to be changed to the following:

The copper and bismuth were separated from antimony by the method given in Section 15, and then the bismuth was separated from the copper by the method given above. The following results were obtained:

TABLE XVII.

Cu.	Bismuth. Present.	Bismuth. Found.	Error. %.
0.26	0.5128	0.5118	—0.20
0.37	0.2589	0.2580	—0.40
0.25	0.2312	0.2318	+0.26

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[1] *Z. anal. Chem.*, **45**, 19 (1906).