

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY].
NEW RESULTS IN ELECTRO-ANALYSIS.¹

BY THOMAS P. MCCUTCHEON, JR.

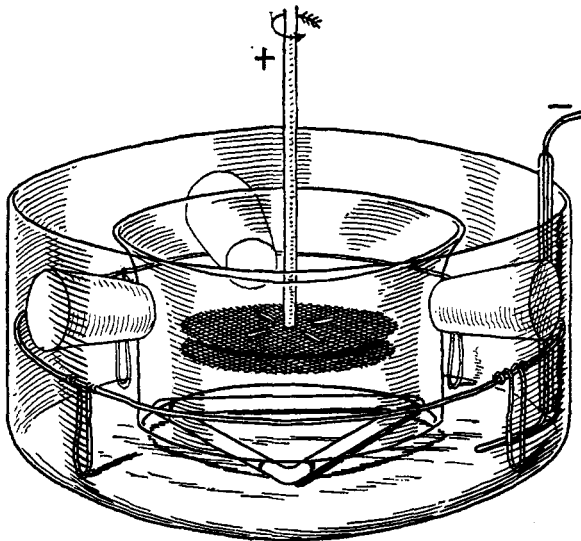
Received August 15, 1907.

Previous workers in electro-chemical analysis have directed their efforts almost entirely to the determination and separation of metals. A year ago, J. H. Hildebrand², working in this Laboratory, showed that such anions as Br, I, PO₄, Fe(CN)₆, CNS could be determined in the electrolytic way. He employed the mercury cathode and an attackable silver anode in a cell especially devised for the purpose. Sodium and potassium can be determined simultaneously, so that a complete analysis of such salts as sodium chloride and potassium ferrocyanide can now be made with ease and accuracy.

The purpose of the first part of this investigation was to extend this work to the estimation of other anions and to learn whether other metals than silver could be advantageously used as anodes. In the second part of the work, the same form of cell was used in the separation of certain metals.

Apparatus.

The decomposition cell, devised by Hildebrand, consisted of a crystallizing dish, the bottom of which was covered with a layer of mercury. In-



side of this was placed a beaker of smaller diameter, without a bottom and supported so that its lower edge extended just below the surface of the mercury. The inner cup was held in position by means of three

¹ From author's thesis for Ph. D. degree, 1907.

² This Journal, 29, 4, 447.

corks placed radially. The mercury was connected with the cathode by means of a stout platinum wire enclosed in a glass tube.

The inner compartment contained the solution to be analyzed. Water was placed in the outer compartment, to which a few drops of sodium chloride solution were added to increase the conductivity and a nickel wire to aid in the decomposition of the amalgam.

The anode consisted of two disks of platinum gauze, placed one above the other and supported by a platinum rod. It was plated with silver by making it the cathode in a bath of silver potassium cyanide. It was then washed, dried and weighed. It was rotated 250-300 times per minute by means of a small motor. The anode was lowered into the inner compartment until the upper gauze was covered by the solution.

The procedure for the analysis of such a salt as sodium chloride was as follows: the salt was placed in the inner compartment and diluted to about 50 cc. and the anode placed in position, while in the outer compartment, as stated above, pure water was placed and a little sodium chloride solution so that the current would be conducted more rapidly at first. On electrolyzing the sodium chloride in the inner compartment, the sodium passed into the mercury and formed an amalgam. In a short time this amalgam found its way into the outer compartment, where it was decomposed with formation of sodium hydroxide. At the conclusion of the experiment the sodium hydroxide was estimated by titration with standard acid, using methyl orange as indicator. The chlorine appeared as silver chloride at the anode and was perfectly adherent. As nothing remained in the inner compartment but pure water, the needle of the ammeter gradually fell almost to zero. This indicated the end of the experiment and the anode was removed, dried and weighed. The increase in weight represented the chlorine in the sodium chloride.

Experimental Part.

On experimenting with other anions than those mentioned above, it appeared that the silver anode was unsatisfactory. In some cases, as with borate and sulphide, the silver salt formed was not perfectly adherent; silver fluoride, on the other hand, was somewhat soluble in water. The following experiments were instituted, with these facts in mind, in the hope that other anodes than silver might prove helpful.

Lead Anode.

The platinum gauzes were plated with lead in a bath of lead sulphocyanide dissolved in potassium hydroxide. In the experiments to be described 4.5 volts were used. This ordinarily gave a current of about 0.5 ampere, falling to 0.02-0.01 ampere when the salt was completely removed from the inner compartment. The anode was rotated 250 times per minute.

Potassium Cyanide.—White lead cyanide formed readily, but did not adhere to the anode.

Borax.—Amperes 0.7-0.03. The lead borate was non-adherent.

Potassium Fluoride.—Amperes 0.7-0.01. After many trials it was again found impossible to obtain a satisfactory deposit. A considerable amount of lead peroxide formed on the anode.

Sodium Sulphate.—Some lead sulphate formed on the anode, but the formation of lead peroxide prevented the estimation of SO_4 . By titrating the caustic soda formed in the outer compartment, it was possible to determine the sodium in the salt with fair results.

	Grams	Amperes	Volts	Time. min.
Sodium sulphate present	0.0852
“ “	0.0276	0.1-0.01	5	3'
“ found	0.0274
	0.0274
	0.0276

Sodium Sulphide.—The lead anode became black as soon as placed in the solution of sodium sulphide. However, as the electrolysis proceeded, pieces of the lead sulphide became detached, making an exact estimation of the sulphur impossible. A curious phenomenon was noticed during this experiment. The solution of sodium sulphide used was quite colorless. In a few minutes the solution in the inner compartment took on a very pronounced yellow color. The same color was noticed when cadmium and bismuth anodes were used with soluble sulphides. The cause of this color will shortly receive further investigation.

Cadmium Anode.

The anode was plated in a bath of potassium cadmium cyanide.

Sodium Sulphide.—The formation of yellow cadmium sulphide became apparent before the current was passed. The solution in the inner compartment became yellow, but after a few minutes became colorless again. The deposit of cadmium sulphide on the anode was adherent, if carefully handled. It was dried in an oven at 115° and weighed. A low voltage should be used and care be taken not to rotate the anode too rapidly; otherwise small pieces of cadmium sulphide may become detached.

	Grams	Volts	Amperes	Time. min.
Sodium sulphide present	0.0429
“ “	0.0252	3.5	0.1-0.03	15
“ found	0.0252
	0.0256
	0.0251

Sodium Chromate.—The cadmium chromate was gelatinous and non-adherent.

Sodium Arsenate.—White cadmium arsenate formed abundantly, but did not adhere to the anode.

Bismuth Anode.

The anode was plated from a solution of bismuth nitrate containing sulphuric acid.

Sodium Chromate.—The color of the liquid in the inner compartment altered from yellow to green and finally a green gelatinous precipitate separated, probably chromium hydroxide. No bismuth chromate formed on the anode.

Sodium Sulphide.—The liquid in the inner compartment again became yellow. When a high pressure was used (14 volts) black bismuth sulphide separated from the liquid. Little bismuth sulphide formed on the anode.

Sodium Arsenate.—No bismuth arsenate appeared, indicating that the bismuth was not attacked by the arsenate anion. The liquid in the inner compartment became acid to litmus, probably due to the formation of arsenic acid.

Sodium Iodide.—The solution in the inner compartment assumed a deep orange color at first. On continuing the electrolysis the color became much paler. The bismuth anode did not change in appearance.

Zinc Anode.

The anode was plated from a solution of sodium zincate.

Sodium Phosphate.—White zinc phosphate formed, but did not adhere.

Sodium Tungstate.—When the anode was rotated slowly, the surface of the mercury in the inner compartment took on a blue iridescent tarnish. No hydrogen was evolved in the outer compartment and the current did not fall. Rapid rotation of the anode caused a slight evolution of hydrogen in the outer compartment and a non-adherent, white, flocculent precipitate, probably zinc tungstate, formed in the inner compartment. In the latter case the current fell from 0.1-0.01 ampere. Five volts were used in each case.

Potassium Cyanate.—A white, non-adherent precipitate formed.

Further a copper anode was used with a solution of sodium arsenite. The green arsenite of copper was formed readily, but little of it adhered to the anode. When an iron anode was used with potassium ferrocyanide, the anode was not attacked and hydroferrocyanic acid seemed to form in the inner compartment.

It is clear, then, that the anodes, described above, behave in several ways toward the different anions. In some cases an insoluble precipitate is formed which may or may not adhere to the anode. In other cases, for example, the iron anode with a soluble ferrocyanide, the anode is not attacked, but the free acid is generated.

These experiments, while not at all exhaustive, seem to indicate that silver is the most suitable anode for receiving most anions. It is entirely

probable that further study will reveal conditions under which the other anodes will give good results.

Electrolysis of Solutions of Metallic Chlorides with a Silver Anode.

Up to this time only salts of sodium and potassium had been electrolyzed in this apparatus. Attention was next turned to other metals, using their chlorides with a silver anode, to learn whether they formed amalgams and whether the amalgams, if formed, decomposed in the outer compartment with formation of hydroxides. A solution of calcium chloride was placed in the inner compartment and electrolyzed in the usual manner. From the appearance of the surface of the mercury it was evident that an amalgam was formed at first, but in a short time it decomposed in the inner compartment, giving rise to a large quantity of calcium hydroxide. H. S. Lukens, working in this laboratory at the same time, found that the amalgams of barium and strontium deported themselves like those of sodium and potassium and decomposed in the outer compartment with formation of hydroxide. He succeeded in making a complete analysis of barium chloride, weighing the chlorine collected at the anode and titrating the barium hydroxide formed in the outer compartment in the manner to be described later. These facts seemed so suggestive that solutions of a number of the metallic chlorides were made up and electrolyzed with the following results:

Amalgams of lithium, sodium, potassium, calcium (see below), strontium and barium decompose in the outer compartment with formation of the corresponding hydroxides.

Amalgams of cadmium, tin, antimony, iron, aluminium, chromium, manganese, zinc, nickel, cobalt, titanium, vanadium, zirconium, thorium, lanthanum, cerium, neodymium, praseodymium, magnesium and uranium decompose in the inner compartment with formation of hydroxides.

Electrolysis of Cerium Chloride. A peculiar result was observed on electrolyzing a solution of cerous chloride. At the beginning the appearance of the surface of the mercury indicated the formation of an amalgam. A subsequent examination proved conclusively that considerable cerium had passed into the mercury. Later the solution in the inner compartment took on a pink color, which finally resembled a somewhat dilute solution of potassium permanganate. This color was observed by transmitted light. It had a greenish, fluorescent appearance by reflected light. The solution was filtered without losing any of its properties. Addition of common salt produced a brownish red precipitate, which differed in appearance both from the hydrated dioxide of cerium, produced by conducting chlorine into an alkaline cerous salt and from the hydrated trioxide, produced by the action of ammonia and hydrogen peroxide on a cerous salt. The precipitate did not dissolve readily in hydrochloric acid, but dissolved in concentrated sulphuric acid with a yellow color.

In this latter respect it resembled the dioxide. The same precipitate formed on allowing the purple solution to stand several days or on continuing the electrolysis for about an hour. A pressure of 8 volts seemed to be most favorable for the formation of this compound. It appeared to be a derivative of cerium in a colloidal condition. A further study of this compound will be made immediately.

Electrolysis of Calcium Chloride. A more careful study was next made of the behavior of calcium chloride in the cell. Lukens found that the salt with which we had been working was contaminated with considerable amounts of magnesium. The calcium was purified by a number of precipitations as oxalate. On electrolyzing the pure chloride, he found that a part of the calcium appeared in the outer compartment like strontium and barium. He was never able to obtain all of it. On mixing magnesium chloride with it again, none of the calcium appeared outside. With these facts in mind, Lukens made a mixture of barium, calcium and magnesium chlorides and was able to completely separate the barium from the calcium and magnesium. A determination by the writer gave the following result :

	Grams.	Volts	Amperes	Time, hours
Barium chloride	0.1049
“ present	0.0691	3.5	0.5-0.02	2
“ found	0.0692	(in presence of calcium and magnesium chlorides.)		

All the previous work had been done with a pressure of 5 volts or under. It seemed probable to the writer that by using a higher voltage, all the calcium could be removed to the outer compartment. The following examples show that such is the case :

	Grams.	Volts	Amperes	Time, hours
Calcium chloride	0.0771
“ present	0.0278	8	0.15-0.02	2
“ found	0.0272
	0.0280
	0.0278
	0.0276
	0.0280

The estimation of the calcium was troublesome at first, as the calcium hydroxide which separated in the outer compartment was not readily soluble in standard acid of convenient strength. The difficulty was removed by adding to the solution in the outer part of the cell a slight excess of standard hydrochloric acid at the beginning of the experiment. At the conclusion the excess of acid was estimated with standard sodium carbonate solution, using methyl orange as indicator.

Separation of Calcium from Magnesium. By using a still higher pressure it was found possible to separate calcium from magnesium, although considerable time was necessary. To remove the last traces of calcium

it was found advantageous to add a drop of hydrochloric acid to the solution in the inner compartment from time to time.

	Grams.	Volt	Amperes	Time, hours
Magnesium chloride	0.1000
Calcium chloride	0.0771	9	0.3-0.02	3
" present	0.0278
" found	0.0282
	0.0276
	0.0281

The calcium hydroxide could be titrated directly in the outer compartment as described above, but to obtain accurate results it was necessary to stir the mercury a long time with a glass rod tipped with a piece of rubber to completely decompose the amalgam. It was found more convenient to remove the anode, siphon out the liquid in the inner compartment with the magnesium hydroxide formed there, and wash the inner compartment thoroughly with pure water. The remaining contents of the cell were then poured into a large beaker. After stirring the mercury well, the titration could be made without difficulty. This procedure was followed in all subsequent analyses where an insoluble hydroxide was formed in the inner compartment.

Separation of Barium and Calcium from Magnesium. The thought occurred that by mixing barium, calcium and magnesium chlorides, it would be possible to remove the barium to the outer compartment with a low pressure, estimate it and then remove the calcium by increasing the pressure. Time did not permit of the completion of this work, but a single determination will show that the separation may be realized :

	Grams.	Volts
Barium chloride	0.1049	...
Calcium " "	0.0771	...
Magnesium " "	0.1000	...
Barium present	0.0691	...
" found	0.0691	3.5
Calcium present	0.0278	...
" found	0.0274	9

Separations.

In view of the fact that the amalgams of the metals divide themselves into two classes, some decomposing in the outer and some in the inner compartment, attention was directed to separations. Obviously there is the possibility of separating any metals in the first class from any metal in the second class and in most of the cases tried the separation proved a success. The only aim in this investigation was to discover whether the separations could be made. No effort was made to reduce the time factor. The experiment was usually begun at two o'clock and stopped between five and six. Nor was an effort made to use larger quantities of the metals. This would materially decrease the percentage

error. In order to work with larger quantities it may be found advantageous to use anodes with a larger surface. These points will be worked out in detail and the most favorable conditions found for each separation.

Separation of the Alkalies and Alkaline Earths from Uranium.

These separations are usually troublesome, and it was thought that an electrolytic separation might be useful.

Sodium from Uranium. No difficulty was experienced in this or the following separation, although the uranium exercised a retarding influence on the sodium. Silver chloride formed on the anode as usual and the inner compartment became full of yellow uranium hydroxide, which later became black. The sodium hydroxide in the outer compartment was titrated with standard hydrochloric or sulphuric acid.

	Grams.	Volts	Amperes	Time, hours
Uranium chloride	0.1000
Sodium chloride	0.1172
“ present	0.0461	3-5	0.5-0.02	3
“ found	0.0463
	0.0459
	0.0457

POTASSIUM FROM URANIUM.

	Grams.	Volts	Amperes	Time, hours.
Uranium chloride	0.1000
Potassium “	0.1467	3-5	0.5-0.01	2
“ present	0.0768
“ found	0.0771
	0.0771
	0.0766

Lithium from Uranium. As lithium chloride had not been previously analyzed in this cell, a solution was made up and electrolyzed with the following results :

	Grams.	Volts	Amperes	Time, hours
Lithium chloride	0.0846
“ present	0.0140	5	0.03-0.02	2
“ found	0.0143
	0.0143
	0.0144

The separation was made as for sodium and potassium from uranium.

	Grams.	Volts	Amperes	Time, hours
Uranium chloride	0.1000	5	0.03-0.02	2
Lithium chloride	0.0846
“ present	0.0140
“ found	0.0143
	0.0142
	0.0141
	0.0141
	0.0142
	0.0143

Barium from Uranium. In this separation the addition of a few drops of hydrochloric acid during the electrolysis was necessary to separate the last traces of barium from the uranium. As under calcium, a slight excess of standard acid was added to the solution in the outer compartment at the beginning of the experiment to prevent the formation of insoluble barium hydroxide. The excess of acid was estimated with standard alkali.

	Grams.	Volts	Amperes	Time, hours
Uranium chloride	0.1000
Barium chloride	0.1040	5	0.15-0.01	1
“ present	0.0685
“ found	0.0685
	0.0688
	0.0682
	0.0682

Strontium from Uranium. In this separation strontium bromide was used.

	Grams.	Volts	Amperes	Time, hours
Uranium chloride	0.1000
Strontium bromide	0.1456	5	0.4-0.02	2
“ present	0.0513
“ found	0.0513
	0.0513
	0.0516
	0.0510

Separation of Barium from Thorium, Cerium, Lanthanum and Neodymium.

The following separations were made to further test the applicability of the method. As before, traces of barium were apt to remain with the hydroxide in the inner compartment unless a few drops of hydrochloric acid were added during the electrolysis.

BARIUM FROM THORIUM.

	Grams.	Volts	Amperes	Time, hours
Thorium chloride	0.1300
Barium chloride	0.1049	5	0.4-0.02	2
“ present	0.0691
“ found	0.0689
	0.0691
	0.0689

BARIUM FROM CERIUM.

	Grams.	Volts	Amperes	Time, hours
Cerium chloride	0.1000
Barium chloride	0.1040	5	0.4-0.02	2
“ present	0.0685
“ found	0.0685
	0.0684
	0.0686

BARIUM FROM LANTHANUM.				
	Grams.	Volts	Ampere	Time, hours
Lanthanum chloride	0.0500
Barium chloride	0.1049	5	0.3-0.01	
“ present	0.0691
“ found	0.0693
	0.0689
BARIUM FROM NEODYMIUM.				
	Grams.	Volts	Amperes	Time, hours
Neodymium chloride	0.1500
Barium chloride	0.1049	5	0.5-0.01	2
“ present	0.0691
“ found	0.0693
	0.0690
	0.0693

Thallium.

The similarity of thallium to the alkalis in many of its behaviors raised the hope that its amalgam would decompose in the outer compartment of the cell. Owing to the insolubility of thallic chloride, the sulphate was used in connection with a lead anode. The platinum gauze was plated with lead in a very satisfactory manner by making it the cathode in a bath of hydrofluosilicic acid. The anode was a strip of pure lead.

When thallic sulphate was electrolyzed in the cell, the solution in the outer compartment soon gave a very distinct test for thallium with potassium iodide. While no quantitative results can be given as yet, it is hoped that thallium can be estimated in this way and its separation from other metals accomplished.

Ammonium Chloride.

A solution of ammonium chloride was electrolyzed with a silver anode. An amalgam was formed in the inner compartment, which swelled up enormously. It was interesting to note that the surface of the mercury in the outer compartment became covered with bubbles and the solution showed a strong alkaline reaction, indicating that the ammonium amalgam had passed to the outer compartment like the amalgams of sodium and potassium.

Electrolysis of a Mixture of Sodium and Potassium Chlorides.

The following experiments were made to ascertain whether larger amounts of chlorine than formerly used could be estimated with the present form of anode. Hildebrand used a solution of sodium chloride containing 0.0708 grams of chlorine. In these determinations double the amount was estimated with an error of less than 0.0005 gram.

The method might be used in the estimation of a mixture of sodium and potassium as chlorides. The mixed chlorides could be weighed, dissolved in water and electrolyzed. The chlorine could be weighed and

the combined sodium and potassium titrated in the outer compartment. The sodium and potassium could be readily calculated from these data.

	Grams.	Volts	Amperes	Time, min.
Sodium chloride	0.1166
Potassium chloride	0.1478	3.5-5	0.5-0.02	45
Chlorine present	0.1416
“ found	0.1420
	0.1420
	0.1418
	0.1420
	0.1414

UNIVERSITY OF PENNSYLVANIA.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY].

THE ELECTROLYSIS OF THE HALIDES OF THE ALKALINE EARTH METALS.

BY HIRAM S. LUKENS AND EDGAR F. SMITH.

Received August 15, 1907.

The studies made by Hildebrand and more recently by McCutcheon with the form of cell pictured and described¹ and in which the rotating silver anode and mercury cathode are employed, led us to try out certain lines of thought in the same way. For example, it seemed worth the while to learn just what quantities of barium chloride, let us say, could be electrolyzed in the Hildebrand cell and the analyst be sure of the accuracy of the results both with respect to the barium and the associated halogen. It was very soon found that quantities of barium chloride exceeding 0.2 gram could be electrolyzed with satisfaction in the course of from forty to sixty minutes with a current of 0.3 ampere and from 3.5 to 4 volts. The anode made 300 revolutions per minute.

The appended results appear in the order in which they were obtained.

Barium present in gram.	Barium found in gram.	Chlorine present in gram.	Chlorine found in gram.
0.2277	0.2276	0.1180	0.1177
0.2277	0.2274	0.1180	0.1178
0.2277	0.2277	0.1180	0.1181
0.2277	0.2278	0.1180	0.1180
0.2277	0.2277	0.1180	0.1180
0.2277	0.2277	0.1180	0.1181

In the electrolysis of strontium bromide, the determination of the bromine was omitted. This halogen adhered firmly to the rotating silver anode to which it attached itself. It was, however, not weighed. The determination of metal alone was made.

Strontium present in gram.	Strontium found in gram.
0.0727	0.0725
0.0727	0.0727
0.0727	0.0727
0.0727	0.0726
0.0727	0.0726

¹ This Journal, 29, 447.