THE RAPID DETERMINATION OF NICKEL AND COBALT BY MEANS OF THE GAUZE CATHODE AND STATIONARY ANODE.

BY RAYMOND C. BENNER AND WILLIAM H. ROSS.

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The use of the gauze electrode as a rapid means of depositing several of the elements has recently been made the subject of a number of investigations. From comparative tests made on the use of this cathode when the solution is rotated by magnetic means as devised by Frary[1] and with the gauze cathode alone, Palmer and Palmer[2] arrived at the conclusion that the gauze electrode, rather than the magnetic rotation of the solution, was the main reason for the success of Frary's method and that this would warrant its use as a simple, rapid means of depositing some of the metals. Stoddard arrived at a similar conclusion a short time previous to this. The work of Frary and Peterson,[3] however, does not exactly confirm these results, for, although comparatively favorable results were obtained in depositing copper on the gauze cathode, yet they are of the opinion that mechanical stirring of the electrolyte may not be generally dispensed with. This is borne out by Price and Humphreys,[4] who conclude from a number of determinations made on several different elements, that for rapid electrochemical analysis, stationary electrodes are not as reliable and satisfactory as rotating electrodes or other means of mechanical agitation of the electrolyte.

Most chemists who have studied this means of deposition have made but a few experiments on each metal, endeavoring to cover the entire field and pass upon the method in general without anything like a thorough study of any one element. The very satisfactory results which were obtained by one of us[5] in the determination of copper and lead with the gauze electrode have led the authors to extend the method to several other metals in different electrolytes in order that the true value of this form of electrode as a rapid means of depositing many of the metals might be established.

The reason for the possibility of the utilization of higher currents with the gauze electrode than with other forms of stationary electrodes appears from the recent work of Blasdell and Cruess[6] and from a few experiments which have been carried on by the authors in connection with other work along this line, to be due to the fact that this form of electrode allows the free circulation of the electrolyte, caused by means of the convection currents set up by the process of electrolysis.

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[1] *Z. Elektrochem.*, 23, 308.

[2] *Trans. Am. Elektrochem. Soc.*, 15, 489 (1909).

[3] May Meeting (1910) American Electrochemical Society.

[4] *J. Soc. Chem. Ind.*, 29, 307.

[5] Benner, *J. Ind. Eng. Chem.*, 2, 195, 348.

[6] THIS JOURNAL, 32, 1264.

Nickel.

Stoddard[1] and Price and Humphreys[1] have each made a few depositions of this element from an ammonium hydroxide solution containing ammonium sulfate in a manner similar to that which we have adopted but did not extend their investigation of this element to include other electrolytes.

In order that a thorough study might be made of the deposition of nickel, a solution of the sulfate was prepared and the nickel content of 10 cc. determined by precipitation with sodium hydroxide and bromine water. The oxide obtained on ignition was reduced to the metal which weighed 0.1808 gram as the mean of five closely agreeing determinations. The nickel content of this solution was also determined by means of the ordinary electrolytic method from an ammonium sulfate electrolyte strongly alkaline with ammonia. The mean of five determinations amounted to 0.1811 gram. The average of the two gave 0.18095 gram as the nickel contained in 10 cc. of the solution.

A second solution used in determining rates of precipitation was standardized electrolytically and found to contain 0.1851 gram of nickel in 10 cc. of the solution.

With these solutions as standards a great many determinations were made for the purpose of comparing the efficiency of the gauze electrode as a means of depositing this metal from the different electrolytes commonly used in the old electrolytic methods. A number of determinations were likewise made in ammonium carbonate solution, concerning which we have been able to find no reference to its use as an electrolyte in the literature. It proved a most satisfactory solution from which to deposit both cobalt and nickel.

The gauze cathodes used in these experiments were cylindrical in shape but of two sizes. The smaller sized cathodes were about 6 grams in weight and made of platinum wire 0.1 mm. in diameter with 26 meshes to the cm. They were 3.5 cm. high by 2.5 cm. in diameter. The corresponding dimensions of the large cathode were 4 cm. by 3.5 cm. and it was made of platinum wire 0.2 mm. in diameter with 18 meshes to the cm. This difference in the size of the cathodes had but little effect on the character of the deposits obtained.

Ammonium Sulfate Electrolyte.—This electrolyte, consisting of ammonium sulfate in ammoniacal solution, is perhaps more commonly used than any other of the older electrolytes. With the gauze electrode the nickel deposited from this electrolyte was almost the color of platinum, very adherent and satisfactory in every respect. In addition to this, the convenience with which the electrolyte can be used makes it one of the most desirable for the determination of this metal. It was not found

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[1] *Loc. cit.*

possible to precipitate nickel from this electrolyte containing much excess of a mineral acid. When the solution was neutral, or slightly ammoniacal, there was a tendency for a deposit to form on the anode. This was entirely prevented by the use of ammonia as directed in the following table, which shows the conditions under which successful determinations were made. When a smaller amount of ammonia is used anodic deposition may be prevented by the addition of glycerol mixture as used by E. F. Smith (5 cc. glycerol, 45 cc. alcohol and 50 cc. water) but this was not found to be as effective as the use of ammonia. It was used, however, in those determinations marked with an asterisk.

Amount taken.	Amount found.	Error. mg.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonium sulfate. grams.	Ammonia, sp. gr. 0.91. cc.	
0.1810	0.1807	−0.3	3	4–5	25	35	3	10	
0.1810	0.1809	−0.1	3	4–5	25	35	3	10	
0.3619	0.3627	+0.8	3	5–6	25	60	3	10	
0.1810	0.1804	−0.6	3	4–5	25	35	3	5	deposit on anode.
0.3619	0.3617	−0.2	3	5–6	20	60	3	10	
0.1810	0.1810	±0.0	3	4–5	25	35	3	5*	no deposit on anode.
0.1810	0.1813	+0.3	4	5–6	20	60	3	5*	
				Rate of precipitation.					
0.1851	0.0833		4	5	2	35	3	10	
0.1851	0.1307		4	5	4	35	3	10	
0.1851	0.1640		4	5	6	35	3	10	
0.1851	0.1836		4	5	12	35	3	10	
0.1851	0.1850		4	5	15	35	3	10	
0.1851	0.1851		4	5	20	35	3	10	

From the rate of precipitation it is seen that it is possible to precipitate 0.1851 gram of nickel in 15 minutes. In this set of experiments as well as in those following, the metal was shown to be completely precipitated in the time given, by careful qualitative tests with ammonium sulfide.

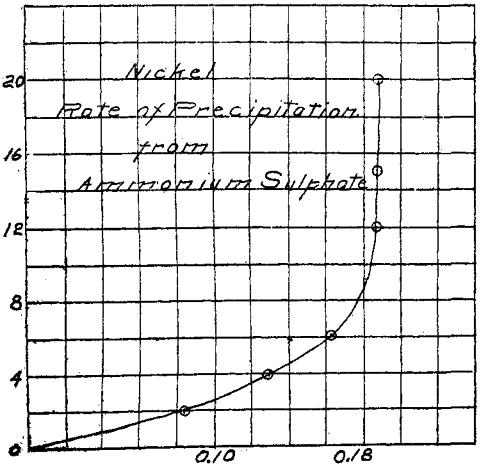

Fig. 1.

Ammonium Acetate Electrolyte. — This electrolyte gave good results under the conditions shown in the table when an excess of ammonia was used. Solutions which contained a slight excess of acetic acid at the beginning of the electrolysis gave good deposits which could scarcely be distinguished in color from the platinum but it was observed that the electrolyte became alkaline as the deposition of the metal proceeded. When enough acid was added to keep the electrolyte acid to the end of the electrolysis the precipitation was either greatly delayed or not complete, and likewise, there was a tendency to anodic deposition. In ammoniacal solution the deposit on the anode can be prevented by the use of sufficient ammonia, or glycerol mixture, as in case of the ammonium sulfate electrolyte. The results tabulated below show that it is possible to precipitate 0.3706 gram of nickel in 20 minutes and likewise the conditions under which good deposits and quantitative results may be expected.

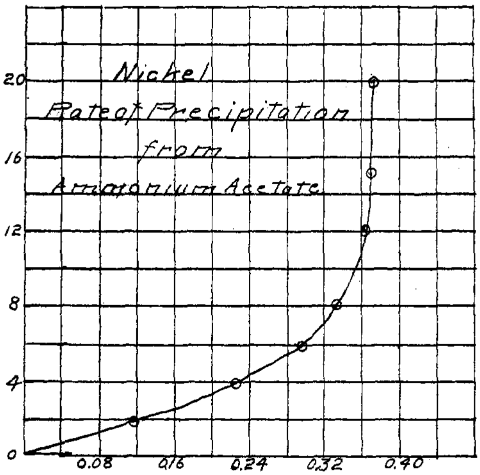

Fig. 2.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Acetic acid, 80 per cent. cc.
0.1810	0.1813	+0.3	3	4–5	25	35	15	5
0.1810	0.1816	+0.6	3	4–5	25	35	15	5
0.3619	0.3618	—0.1	4	5–6	20	60	15	5
0.3619	0.3624	+0.5	4	5–6	20	60	15	5
0.3619	0.3625	+0.6	4	5–6	20	60	15	5
0.1810	0.1801	—0.8	3	4–5	25	35	20	10
0.1810	0.1813	+0.3	3	4–5	25	35	2	slightly acid with acetic acid*
0.1810	0.1816	+0.6	3	4–5	25	35	2	slightly acid with acetic acid*
0.1810	0.1811	+0.1	3	5	25	60	2	slightly acid with acetic acid*
0.3619	0.3623	+0.4	3	5	25	60	2	slightly acid with acetic acid*
0.1810	0.1808	+0.2	3	4–5	15	35	2	slightly acid with acetic acid*

Rate of precipitation.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Acetic acid, 80 per cent. cc.
0.3702	0.1159		4	5–6	2	60	15	5
0.3702	0.2231		4	5–6	4	60	15	5
0.3702	0.3337		4	5–6	8	60	15	5
0.3702	0.3630		4	5–6	12	60	15	5
0.3702	0.3659		4	5–6	15	60	15	5
0.3702	0.3706		4	5–6	20	60	15	5
0.3702	0.3706		4	5–6	25	60	15	5

Sodium Acetate Electrolyte.—The deposition of nickel from a solution of sodium acetate containing free acetic acid was quite satisfactory. The deposits had the color of platinum and were perfectly adherent. The electrolyte became alkaline when a neutral or very slightly acid solution was used but unlike the results obtained with the ammonium acetate electrolyte it was found that the deposition of the metal from a solution which remained acid to the end of the electrolysis was only slightly retarded. Glycerol mixture was used to prevent anodic deposition.

Amount taken.	Amount found.	Error.	Amperes	Volts.	Time. Minutes.	Volume of solution. cc.	Sodium acetate. Grams.	Acetic acid, 80 per cent. cc.
0.1810	0.1816	+0.6	3	6–7	30	35	2	2*
0.1810	0.1814	+0.4	3	6–7	35	35	2	2*
0.1810	0.1815	+0.5	3	6–7	35	35	2	2*
0.1810	0.1816	+0.6	3	6–7	30	35	2	1.5*
0.1851	0.1856	+0.5	3	6–7	30	35	2	2*
0.3702	0.3707	+0.5	3	6–7	30	35	2	2*

Ammonium and Sodium Formate Electrolytes.—The deposition of nickel from ammonium formate in alkaline solution, and sodium formate in both acid and alkaline solutions has been tried with results similar to those obtained with ammonium and sodium acetate under corresponding conditions.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia sp. gr. 0.91. cc.	Formic acid. 1.06 sp. gr. cc.
0.1810	0.1811	+0.1	3	5–6	25	60	2	slight excess*
0.1810	0.1806	—0.4	3	4–5	30	35	15	5
0.1810	0.1808	—0.2	3	4–5	30	35	15	5
0.3619	0.3621	+0.2	3	4–5	30	35	15	5
0.3619	0.3624	+0.5	4	5–6	30	60	15	5
0.3619	0.3618	—0.1	4	5–6	20	60	15	5
0.1810	0.1814	+0.4	4	4–5	20	35	15	5
							Sodium carbonate, gram.	
0.1810	0.1807	—0.3	3	6–7	30	60	1	2 excess*
0.1810	0.1811	+0.1	3	6–7	30	60	1	2 excess*
0.1810	0.1803	—0.7	4	6–7	30	60	1	2 excess*
0.1810	0.1806	—0.4	3	5–6	30	35	1	2 excess*
0.1810	0.1815	+0.5	3	5–6	30	35	2	2 excess*
0.1810	0.1813	+0.3	3	5–6	35	35	2	2 excess*
0.1810	0.1815	+0.5	3	5–6	25	35	2	2 excess*

Ammonium Carbonate Electrolyte.—The results obtained from a solution of ammonium carbonate were usually a little too high. By adding a few cc. of ammonium hydroxide the high results were prevented and excellent deposits obtained in all cases.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonium carbonate. Grams.	Ammonia, sp. gr. 0.91. cc.
0.1851	0.1851	±0.0	4	5–6	20	35	4	10
0.1851	0.1853	+0.2	4	5–6	20	35	4	10
0.1851	0.1857	+0.6	4	5–6	20	35	4	5
0.1851	0.1850	—0.1	4	5–6	20	35	4	5
0.3620	0.3624	+0.4	4	5–6	20	60	4	10
0.3620	0.3630	+1.0	4	5–6	20	60	4	10
			Rate of precipitation.					
0.1851	0.0825		4	5–6	2	35	4	5
0.1851	0.1430		4	5–6	4	35	4	5
0.1851	0.1681		4	5–6	6	35	4	5
0.1851	0.1803		4	5–6	8	35	4	5
0.1851	0.1823		4	5–6	10	35	4	5
0.1851	0.1846		4	5–6	12	35	4	5
0.1851	0.1855		4	5–6	20	35	4	5

Ammonium Oxalate Electrolyte.—Nickel can be deposited from a solution of ammonium oxalate containing a slight excess of mineral acid, from a neutral solution and also from a solution alkaline with ammonium hydroxide. The results obtained from neutral and acid solutions were nearly always high, probably due to the deposition of carbon. In alkaline solutions this was not quite so marked. The deposits were bright in color and perfectly adherent. Because of its comparatively low solubility, this electrolyte, however, is not as convenient to use as some of the others.

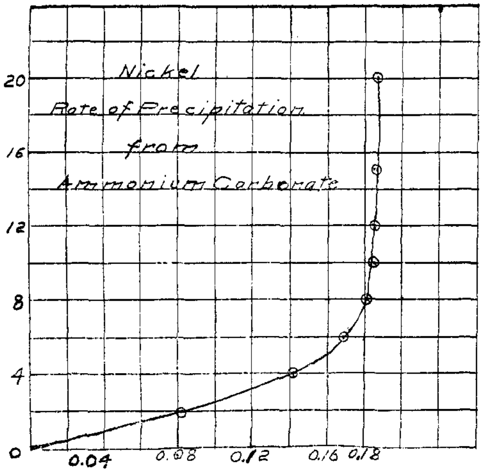

Fig. 3.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonium oxalate. Grams.	Ammonia, sp. gr. 0.91. cc.
0.1810	0.1805	—0.5	4	5–6	25	60	3	10
0.1810	0.1812	+0.2	3	4–5	25	30	3	10
0.3620	0.3629	+0.9	4	5–6	20	60	4	5
0.3620	0.3623	+0.3	4	5–6	20	60	4	5
0.1851	0.1847	—0.4	4	5–6	20	60	4	5
0.1810	0.1819	+0.9	4	4–5	20	30	4	10
0.1810	0.1823	+1.3	4	4–5	20	30	4	10
0.1810	0.1817	+0.7	4	4–5	20	30	4	10

Potassium Cyanide Electrolyte.—A number of careful experiments were made with potassium cyanide as an electrolyte but satisfactory results could not be obtained with the high currents used. When preparing this electrolyte a dilute solution of potassium cyanide was carefully added to the nickel solution, from a buret, drop by drop, until the precipitate, which first formed, redissolved. A few drops were then added in excess. As the electrolysis proceeded the cyanide was decomposed with the result that nickel was precipitated.

Cobalt.

The rapid deposition of cobalt has not been made so far by means of the gauze cathode, with stationary anode. The solution of cobalt sulfate used in the following experiments was standardized first by the old electrolytic method from an electrolyte containing ammonia and ammonium sulfate. As a mean of five closely agreeing determinations, 10 cc. of the solution were found to contain 0.1052 gram of cobalt. When the solution was made acid with sulfuric acid, evaporated and weighed as the sulfate, the residue corresponded to 0.1050 gram of cobalt. This gave 0.1051 gram as the mean of the two methods for the nickel content of the solution.

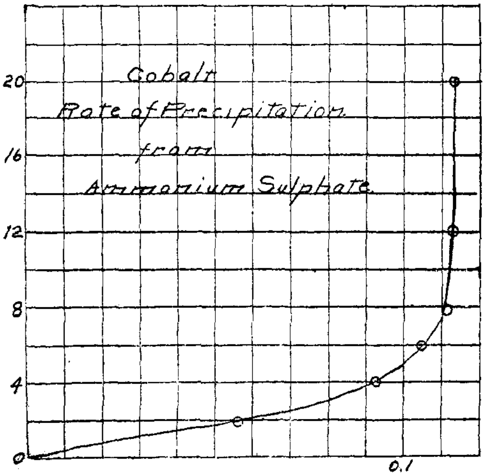

Fig. 4.

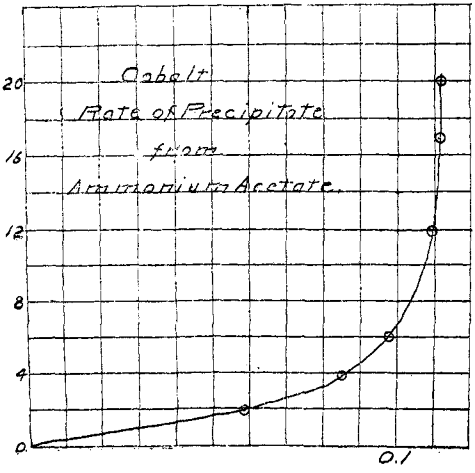

Fig. 5.

Ammonium Sulfate Electrolyte.—The use of this electrolyte in the rapid precipitation of cobalt gave as satisfactory results as were obtained in case of nickel in neutral or slightly alkaline solutions. Cobalt had a tendency to form deposits on the anode. This, however, was not as marked as in case of nickel and could be prevented in a similar manner, by the use of glycerol mixture or by the addition of strong ammonia. The deposits obtained were dark colored but perfectly adherent and in every way satisfactory. As shown in the table complete precipitation could be made in 15 minutes from a solution containing 0.1125 gram of cobalt.

Amount taken	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Ammonium sulphate. Grams.
0.2102	0.2102	±0.0	3–4	5–6	30	65	10	6
0.2102	0.2108	+0.6	3–4	5–6	30	65	10	6
0.1051	0.1055	+0.4	4–5	5–6	20	35	10	3
0.1051	0.1052	+0.1	4–5	5–6	20	35	10	3
0.2102	0.2101	—0.1	7	6–8	18	40	10	3
0.2102	0.2104	+0.2	7	6–8	18	40	10	3
0.2102	0.2104	+0.2	6–7	6–8	20	65	10	3
0.1051	0.1050	—0.1	5–6	6–7	20	35	10	3
			Rate of precipitation.					
0.1125	0.0547		4	6	2	35	10	3
0.1125	0.0968		4	6	4	35	10	3
0.1125	0.1048		4	6	6	35	10	3
0.1125	0.1109		4	6	8	35	10	3
0.1125	0.1122		4	6	12	35	10	3
0.1125	0.1120		4	6	20	35	10	3

Ammonium Acetate Electrolyte.—Ammonium acetate was not only a very convenient electrolyte to use but the deposits obtained were moderately bright and perfectly adherent. The same results were obtained in acid solution as were noted for nickel. In this as well as in the ammonium sulfate electrolyte the tendency of the cobalt to deposit on the anode was less marked than was observed in the case of nickel and did not occur under the conditions given in the table.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Acetic acid, 80 per cent. cc.
0.1051	0.1050	—0.1	4–5	5–6	30	35	15	5
0.1051	0.1047	—0.4	4–5	5–6	30	35	15	5
0.2102	0.2100	—0.2	4–5	6–7	35	60	20	10
0.1051	0.1055	+0.4	3–4	4–5	35	40	20	10
0.2102	0.2100	—0.2	4–5	6–7	20	60	20	10
0.1051	0.1045	—0.6	3–4	4–5	25	35	15	5
0.1051	0.1055	+0.4	3–4	4–5	25	35	5	5*
0.1051	0.1048	—0.3	3–4	4–5	25	35	5	5*
			Rate of precipitation.					
0.1125	0.0594		4	5	2	35	15	5
0.1125	0.0848		4	5	4	35	15	5
0.1125	0.0978		4	5	6	35	15	5
0.1125	0.1096		4	5	12	35	15	5
0.1125	0.1111		4	5	17	35	15	5
0.1125	0.1125		4	5	20	35	15	5
0.1125	0.1127		4	5	25	35	15	5

Sodium Acetate Electrolyte.—The results obtained with this electrolyte were comparable in all respects to those obtained with nickel. The deposits formed in acid solutions were brighter than those obtained in ammoniacal solution. The retarding effect of different amounts of acid may be seen by referring to the table.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time Minutes.	Volume of solution. cc.	Sodium acetate. Grams.	Acetic acid, 80 per cent. cc.
0.1125	0.1127	+0.2	3	6–8	30	35	2	1.5
0.1125	0.1125	0.0	3	6–8	35	35	2	2.0
0.1125	0.1129	+0.4	3	6–8	35	35	2	1.5
0.1125	0.1127	+0.2	3	6–8	25	35	2	1.5
0.1125	0.1121	—0.4	3	6–8	30	35	2	2.0
0.1125	0.1127	+0.2	3	6–8	25	35	2	1.5
0.2250	0.2190		3	7	15	35	2	1.0
0.2250	0.2111		3	7	15	25	2	2.0
0.2250	0.1995		3	7	15	25	2	3.0
0.2250	0.1825		3	7	15	35	2	5.0
0.2250	0.1629		3	7	15	35	2	10.0
Rate of precipitation.								
0.2250	0.0572		3	7	2	35	2	3
0.2250	0.0982		3	7	4	35	2	3
0.2250	0.1176		3	7	6	35	2	3
0.2250	0.1434		3	7	8	35	2	3
0.2250	0.1823		3	7	12	35	2	3
0.2250	0.2130		3	7	20	35	2	3
0.2250	0.2235		3	7	25	35	2	3
0.2250	0.2243		3	7	30	35	2	3
0.2250	0.2245		3	7	40	35	2	3

Sodium and Ammonium Formate Electrolyte.—These electrolytes gave good results, under the same conditions as have already been described in the use of the sodium and ammonium acetate electrolytes.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Formic acid, sp. gr. 1.06. cc.
0.1051	0.1051	±0.0	4	5–6	20	35	15	5
0.2102	0.2095	—0.7	4	5–6	20	35	15	5
0.2102	0.2110	+0.8	4	5–6	25	35	7	5*
0.1051	0.1055	+0.4	3–4	5–6	25	35	7	5*
0.1051	0.1056	+0.5	3–4	5–6	25	35	7	5*
0.1051	0.1059	+0.8	3–4	5–6	25	35	7	5*
Rate of precipitation.								
0.2250	0.0911		4	5–6	2	35	10	5
0.2250	0.1544		4	5–6	4	35	10	5
0.2250	0.1942		4	5–6	6	35	10	5
0.2250	0.2142		4	5–6	8	35	10	5
0.2250	0.2229		4	5–6	12	35	10	5
0.2250	0.2236		4	5–6	15	35	10	5
0.2250	0.2247		4	5–6	20	35	10	5
							Sodium carbonate. Grams.	
0.1125	0.1123	—0.2	3	6–7	35	35	2	2 excess*
0.1125	0.1126	+0.1	3	6–7	35	35	2	2 excess*
0.1125	0.1124	—0.1	3	6–7	35	35	2	2 excess*
0.1125	0.1124	—0.1	3	6–7	35	35	1	3 excess*
0.2250	0.2240	—1.0	3	6–7	35	35	1	3 excess*

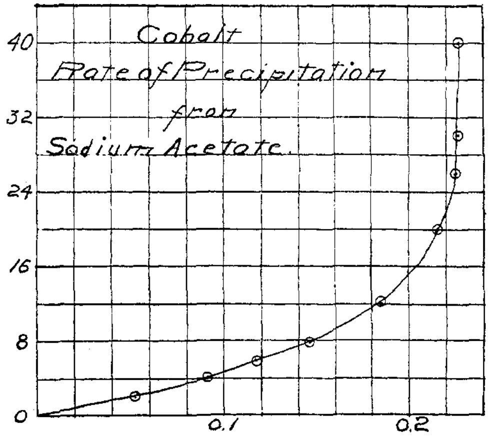

Fig. 6.

Ammonium Carbonate Electrolyte.—The precipitation of cobalt from this new electrolyte was attended with uniform success. The deposits were invariably good and there was no tendency to anodic deposition either with or without the addition of ammonia to the solution. This fact makes this electrolyte one of the most satisfactory which we have used. As the standard cobalt solution was slightly acid, an excess of ammonia was usually added before the carbonate to prevent loss by effervescence.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0.91. cc.	Ammonium carbonate. Grams.
0.1051	0.1055	+0.4	3–5	5–6	25	35	5	5
0.1051	0.1052	+0.1	3–5	5–6	25	35	5	5
0.1051	0.1054	+0.3	3–5	5–6	23	35	5	5
0.1051	0.1052	+0.1	3–5	5–6	23	35	5	4
0.2102	0.2096	—0.6	3–5	5–6	25	35	5	6
0.2102	0.2096	—0.6	3–5	5–6	25	35	5	6
0.1051	0.1049	—0.2	4	5–6	20	35	5	4
0.1051	0.1056	+0.5	4	5–6	20	35	5	4
				Rate of precipitation				
0.1125	0.0594		4	5–6	2	35	5	5
0.1125	0.0908		4	5–6	4	35	5	5
0.1125	0.1054		4	5–6	6	35	5	5
0.1125	0.1092		4	5–6	8	35	5	5
0.1125	0.1119		4	5–6	10	35	5	5
0.1125	0.1125		4	5–6	15	35	5	5
0.1125	0.1123		4	5–6	20	35	5	5

Ammonium Oxalate Electrolyte.—The results with ammonium oxalate, which is a standard electrolyte in the older electrolytic methods, were usually a little low. This held true whether the solution was slightly acid with a mineral acid, neutral or alkaline with ammonia. This was found to be due to a small amount of the cobalt being precipitated during the electrolysis, and which was not redissolved during the time usually allowed for the determination. This result, together with the fact that the ammonium oxalate can not be as conveniently used as the other electrolytes, because of its low solubility, makes it an electrolyte which cannot be recommended for the rapid determination of cobalt on the gauze electrode.

Amount taken.	Amount found.	Error.	Amperes.	Volts.	Time. Minutes.	Volume of solution. cc.	Ammonia, sp. gr. 0 91. cc	Ammonium oxalate. Grams.
0.1051	0.1051	±0.0	4–5	6–7	20	35	....	4
0.1051	0.1051	±0.0	4–5	6–7	20	35	....	4
0.1051	0.1041	—1.0	4–5	6–7	20	35	....	4
0.1051	0.1046	—0.5	4–5	6–7	20	35	....	4
0.1051	0.1043	—0.8	3–5	5–6	20	35	5	3
0.1051	0.1045	—0.6	3–5	5–6	20	35	5	3

Potassium Cyanide Electrolyte.—The same negative results were obtained in the deposition of cobalt with this electrolyte as were noted for nickel.

Conclusion.

1. The rapid determination of nickel and cobalt by means of the gauze electrode and stationary anode is perfectly satisfactory with most of the electrolytes in common use.

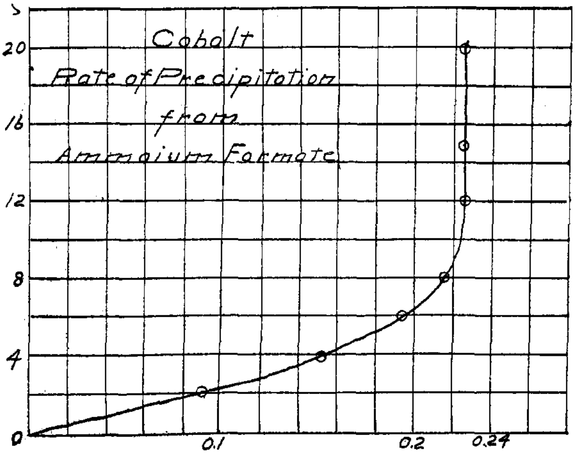

Fig. 7.

2. The rate at which they are precipitated is practically the same for all of the electrolytes which can be used in ammoniacal solution and is little affected by the amount of ammonia added. In acid solution the rate of precipitation is not quite as great as in ammoniacal solution and decreases slightly as the amount of acid is increased.

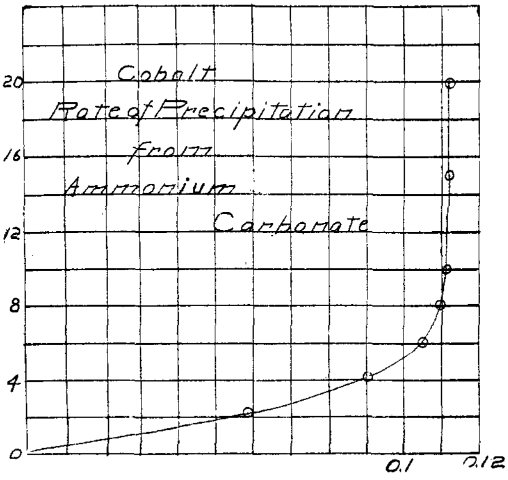

Fig. 8.

3. Although the rate of precipitation of these elements on the gauze electrode is not quite equal to the rate at which they are precipitated by means of the same current when the electrolysis is agitated by mechanical means, it is rapid

enough for practical purposes and much more satisfactory on account of the simplicity of the apparatus and the fact, that, when desired, the older methods with small currents may be used with the same electrode, and without alteration of the rest of the apparatus.

UNIVERSITY OF ARIZONA,
TUCSON.

SENSITIVENESS OF THE COLORIMETRIC ESTIMATION OF TITANIUM.[1]

BY ROGER C. WELLS.

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The color produced by hydrogen peroxide in titanium solutions serves for the estimation of small amounts of titanium and also, through a bleaching effect upon it, for small quantities of fluorine. At first thought one might suppose that there would be a concentration of maximum accuracy for this estimation, but it has been shown that there is in general a wide range of concentration over which the accuracy of a colorimetric comparison remains practically constant.[2] The object of the experiments here described was to establish the range of suitable concentrations in the case of titanium.

In any colorimetric comparison there is a limit to the difference of shade, or rather the difference in intensity of color, which the eye can detect. One may prepare two known solutions, one of which will be just perceptibly stronger in color, the other just perceptibly weaker than a given unknown solution. The difference in concentration of the two extremes, divided by 2, will be a certain *fraction* of the mean total substance present, and this fraction, expressed as a percentage, may be said to represent the maximum error of the comparison, or the *perceptible difference.* In comparing two solutions by a single setting, it is evident that the setting may fall anywhere between the two limits. Hence an average of several readings is essential. An equally good procedure is to determin the two limits and take the mean as the correct reading.

It was sought to determin the "perceptible differences" for various titanium solutions. The comparisons were made in the colorimeter devised by George Steiger, of the U. S. Geological Survey.[3] Instead of preparing many solutions the comparisons were made by sliding one of the cells. Scale distances were taken as proportional to concentrations. One cell was set to read 10, the other was set to appear either stronger or weaker as the case might be. After alternately resting the eyes and observing the cells a number of times, when a plurality of observations indicated that there was a difference in intensity, the position was noted.

[1] Published by permission of the Director of the U. S. Geological Survey.

[2] D. W. Horn and Sue A. Blake, *Am. Chem. J.*, 36, 202 (1906).

[3] THIS JOURNAL, 30, 215 (1908).