

1:13.5 at 2.0 molar) as the concentration of the latter decreases, but finally attains at a moderate dilution (about 0.025 molar) a nearly constant value (1:20.2).

(7) That the solubility of silver bromide as previously found by Bodländer and Fittig is proportional to the concentration of the ammonia between the limits of 0.08 and 0.45 molar, and that the ratio has the value 1:289. The constancy of this ratio is in correspondence with the requirement of the formula  $\text{Ag}_n(\text{NH}_3)_{n+1}\text{Br}_n$ .

(8) That the ratio of the solubilities in dilute ammonia of silver oxide and chloride is the same as the ratio of their solubilities in water, as the formula  $\text{Ag}(\text{NH}_3)_2\text{R}'$  alone requires.

(9) That the solubility of silver bromide in water at  $25^\circ$ , is found to be  $0.99 \times 10^{-6}$  and  $0.95 \times 10^{-6}$  when calculated under the assumption of proportionality, from the relative solubilities in ammonia of silver bromide and oxide on the one hand and of silver bromide and chloride on the other.

(10) That the solubility of silver oxide in ammonia is much greater at  $0^\circ$  than at  $25^\circ$ , though the reverse is true of its solubility in pure water; and that this is due to a much slighter dissociation-tendency of the complex ion into its components at the lower temperature.

It is our agreeable duty at this point to express our sincere thanks to Prof. A. A. Noyes for his very considerable assistance and continual interest in this investigation.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,  
BOSTON, September, 1902.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY,  
No. 67.]

## THE ELECTROLYTIC ESTIMATION OF BISMUTH AND ITS SEPARATION FROM OTHER METALS.<sup>1</sup>

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### INTRODUCTION.

IN determining bismuth by the ordinary gravimetric methods many difficulties confront the analyst. These limitations led the author to give attention to the estimation of this metal in the electrolytic way.

<sup>1</sup> From the author's thesis for the degree of Ph.D., 1901.

A careful study of the literature was made and all the methods thus far proposed for the electrolytic estimation of bismuth were carefully considered. It was observed that frequent and numerous attempts had been made to determine it electrolytically. As far back as 1840 Cozzi separated bismuth together with other metals from animal fluids. In 1862 Nickels and, three years later, Luckow described methods for its qualitative detection in the presence of other metals. In 1880 Ludwig Schlucht published an important series of investigations on its behavior in electrolysis. From this time on methods for its quantitative estimation began to appear, Luckow, Smith and Classen being the first to do work in this direction. The methods that have been proposed are numerous and diverse in character.<sup>1</sup> The metal has been deposited from oxalic acid and ammoniacal citrate solutions, also from nitric acid, sulphuric acid and phosphoric acid solutions. Mixed electrolytes containing alkaline pyrophosphates, carbonates and oxalates have been employed. Vortmann recommends that the bismuth be deposited together with mercury as an amalgam. More recently Karl Wimmenauer modified the old nitric acid method by introducing glycerine and making use of a revolving anode.

No one of the methods proposed can be said to be entirely free from objection. In fact so doubtful is the successful determination of bismuth electrolytically that Classen does not deem it advisable to describe even one method in the last edition of his book, "Analysis by Electrolysis." Under the heading of bismuth, he merely states, that up to the present time it has been found impossible to precipitate bismuth quantitatively in compact, metallic form.

This lack of success is to be attributed mainly to two causes: (1) the non-obtainment of a dense adherent metallic deposit and (2) the formation of superoxide of bismuth on the anode. The very few methods for which it is claimed that these difficulties have been surmounted introduce other limitations and features quite undesirable, such as the use of very small quantities of metal,

<sup>1</sup> Literature.—Luckow: *Ztschr. anal. Chem.*, **19**, 16; Classen and v. Reiss: *Ber. d. chem. Ges.*, **14**, 1622; Thomas and Smith: *Am. Chem. J.*, **5**, 114; Moore: *Chem. News*, **53**, 209; Smith and Knerr: *Am. Chem. J.*, **8**, 206; Schlucht: *Ztschr. anal. Chem.*, **22**, 492; Eliasberg: *Ber. d. chem. Ges.*, **19**, 326; Brand: *Ztschr. anal. Chem.*, **28**, 596; Vortmann: *Ber. d. chem. Ges.*, **24**, 2749; Rüdorff: *Ztschr. angew. Chem.* (1892), p. 199; Smith and Salter: *Ztschr. anorg. Chem.*, **3**, 418; Smith and Moyer: *This Journal*, **15**, 28; *Ibid.*, **15**, 101; Kollock: *This Journal*, 1899; Wimmenauer: *Ztschr. anorg. Chem.*, **27**, 1.

the employment of unusual and involved apparatus and the use of solutions difficult to obtain or solutions which do not lend themselves well to the separation of bismuth from other metals. None of these methods offer any advantages over the ordinary analytical methods.

It was with the hope of overcoming these difficulties and eliminating the objectionable uncertainties which always attend the electrolytic determination of bismuth by any of the described methods that the present investigation was undertaken.

*Apparatus.*—The apparatus used in this work was that usually employed in electrolysis. As cathodes platinum dishes were used of the ordinary shape, having a cathode surface of 100 sq. cm. when containing 150 cc. of liquid. Some had polished interior surfaces, others had their interior surfaces roughened (sand-blasted). Larger dishes, having a capacity of 250 cc., and a cathode surface of 200 sq. cm., were also employed.

The anodes were of two styles, ordinary flat spirals of two turns of stout platinum wire, having an anode surface of 4.5 sq. cm. and basket anodes, having an anode surface of 60 sq. cm. The latter style of anodes has the same shape as the platinum dish which is used as the cathode and is perforated with quite a number of holes to allow free circulation of the electrolyte.

Platinum gauze electrodes were also experimented with. They were in the shape of upright cylinders 5 cm. high and 10 cm. in circumference, the anode surrounding the cathode, and each having an electrode surface of 10 sq. cm. They dipped, or rather, were immersed, into the electrolyte contained in a beaker-glass of 300 cc. capacity.

The advantages offered by gauze electrodes are, briefly, that a very uniform current density is obtained all over the electrode, and therefore a uniform deposit of metal, that the deposit entirely surrounds the wire and, therefore, cannot readily peel off, and finally, that larger currents can be employed, thus reducing the time of deposition.<sup>1</sup>

The current used in these depositions was derived from storage cells.

The heating of the electrolyte was accomplished by means of a

<sup>1</sup> Cf. Winkler: *Ber. d. chem. Ges.*, **32**, 2192; also *Ztschr. anal. Chem.*, **39**, 517.

very small flame of a Bunsen burner. A sheet of asbestos placed a quarter of an inch below the dish shielded it from the direct flame of the burner.

During the electrolysis the dishes were kept covered with cover-glasses having two perforations ground into them. Through one passed the connecting wire of the anode and through the other hung a thermometer which dipped into the electrolyte during the whole deposition so that the temperature could be closely watched.

#### SOLUTION.

Sulphuric acid, of all the available solutions from which to deposit the metal, seemed to offer the greatest advantages and was therefore selected. As early as 1883 Thomas and Smith<sup>1</sup> and in 1886 Smith and Knepp<sup>2</sup> worked with this electrolyte and with considerable success, but as this was before the introduction of precise measurement of current strength and voltage into electrolytic work, their conditions as to these points are not very definitely stated. In these experiments they limited themselves to the employment of small quantities of metal, which is objectionable as it increases the percentage error.

Having selected sulphuric acid, attention was first directed toward obtaining a solution of bismuth sulphate. The great insolubility of the sulphate and the strong tendency of the dissolved sulphate to form insoluble basic sulphates were difficulties not easily overcome, and the simple sulphate solution was soon abandoned as impracticable. Two determinations, however, were made from simple sulphuric acid solutions obtained as follows: a weighed quantity of bismuth oxide was dissolved in a few cubic centimeters of nitric acid and then evaporated down with concentrated sulphuric acid until fumes appeared, when it was diluted with water and electrolyzed.

In all the subsequent determinations definite volumes of a standardized nitric acid solution of bismuth were employed. The solution was made up as follows: 20 grams (approximately) of bismuth subnitrate were dissolved in 100 cc. of nitric acid (sp. gr. 1.42) and this solution diluted to 1 liter with water. The bismuth content of the solution was then ascertained by cautiously evapo-

<sup>1</sup> *Am. Chem. J.*, 5, 114.

<sup>2</sup> *Ibid.*, 8, 206.

rating 20 cc. to dryness in a porcelain crucible and igniting to bismuth oxide ( $\text{Bi}_2\text{O}_3$ ) and weighing as such. 10 cc. of such a solution will contain from 0.10 to 0.15 gram of bismuth and 1 cc. of nitric acid.

#### EXPERIMENTAL PART.

Definite volumes of the standardized bismuth solution were electrolyzed in the presence of free sulphuric acid and an alkali sulphate, the dilution being usually 150 cc.

The effect of the quantity of sulphuric acid on the deposition was studied, also the influence of different alkali sulphates in varying amounts. Further, the effect of variations in the temperature, cathode surface, current density, dilution, and the style of the electrodes received careful consideration. The quantity of nitric acid was also varied and its effect noted.

After making quite a number of experiments in the variation of the quantity of sulphuric acid, 2 cc. of acid of specific gravity 1.84 were found to give the best results. When more acid than that is used it has a solvent influence on the deposited bismuth and makes it almost impossible to precipitate the last traces of the metal.

The presence of an alkali sulphate in solution was found to be essential for obtaining good metallic deposits. In the presence of sulphuric acid alone the metal does not deposit in good form nor completely. Sodium, potassium and ammonium sulphates were experimented with; of the three, potassium sulphate yielded the best results, 1 gram being the most favorable quantity. Sodium sulphate, however, can be used and good results be obtained. In the presence of ammonium sulphate bismuth is deposited in beautiful form, but there is a tendency to superoxide deposition on the anode. Very little of the latter indeed separates, but the slightest quantity is enough to be considered objectionable. The use of ammonium sulphate is therefore not to be recommended.

Larger quantities of nitric acid than that introduced with the standard bismuth solution were found to be objectionable, causing the bismuth to come down loose and black.

It was found that the temperature has considerable influence on the character of the deposit. In the cold it is impossible to precipitate the bismuth in a compact metallic form. On the other hand, when heated to a temperature as high as  $70^\circ$  the electrolyte

exerts a solvent action on the bismuth deposited, making it difficult to completely precipitate the metal. Another objection to high temperatures is the formation of gas bubbles on the bottom of the dish. The bismuth deposits about these in loose, black, spongy masses, which readily become detached and are lost in washing the deposits. If bubbles are noticed, it is advisable to gently tap the dish with the finger, causing them to rise to the surface.

A temperature of from  $45^{\circ}$  to  $50^{\circ}$  C. was found to be the most favorable. Roughened cathode surfaces are not advantageous, the bismuth depositing better on polished surfaces.

In all the depositions it was found absolutely necessary to employ a low current strength, especially during the first part of the deposition until most of the metal was precipitated. If a current, much exceeding 0.03 ampere was used as the initial current, the bismuth invariably came down dark and loose. Experiment showed a current strength of 0.02 to 0.05 ampere, depending on the style of electrodes, to be the proper one, the voltage ranging from 1.8 to 2.0 volts. Toward the end of the deposition, when most of the metal has been deposited, the current can be increased to 0.10 to 0.15 ampere to bring down the last traces of bismuth.

The following tables contain the results of determinations made from the different electrolytes after the most favorable conditions for each had been worked out by previous experiments.

Most of the deposits obtained in these determinations were very metallic in appearance, steel-gray in color, usually having the pinkish tinge or caste so characteristic of metallic bismuth. Often the deposited metal was quite crystalline.

The following is a brief statement of the most favorable conditions:

- 0.10 to 0.15 gram of metal dissolved in 1 cc. of nitric acid (sp. gr. 1.42.)
- 2 cc. of sulphuric acid (sp. gr. 1.84.)
- 1 gram of potassium sulphate.
- 150 cc. total dilution.
- Time, 8 to 9 hours.
- Temperature,  $45^{\circ}$  to  $50^{\circ}$  C.
- N.D.<sub>100</sub> = 0.02 ampere.
- Volts 1.8.

During the last hour the current strength should be increased

## BISMUTH FROM SODIUM SULPHATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Grams.	Dilution. Cc.	Temperature. °C.	Time. Hours.	N.D. 100. Ampere.	Voltage. Volts.	Style of cathode.	Character of the deposit.
0.1182	0.1186	2	1	125	50	7½	0.03	1.7	smooth	steel-gray, pink tinge.
0.1182	0.1177	3	1	125	52	7	0.03	1.7	"	"
0.1182	0.1190	2	1	125	51	5	0.025	1.7	"	light gray, few black spots.
0.1182	0.1184	2	1	125	55	6½	0.025	1.8	"	same
0.1182	0.1186	2	1	125	43	7	0.02	1.7	"	very light and metallic.
0.1182	0.1177	2	1	125	50	7	0.02	1.7	rough	light gray and metallic.
0.1182	0.1178	2	2	125	45	7¾	0.02	1.7	smooth	" " with few spots.
0.1182	0.1179	3	1	125	53	6¾	0.02	1.7	"	" " with pink tinge.
0.1182	0.1186	2	1	125	53	7	0.02	1.8	rough	"
0.1182	0.1193	2	1	125	60	8	0.02	1.8	smooth	"
0.1182	0.1180	3	1	125	55	7	0.02	1.7	rough	"
0.1182	0.1180	2	1	125	52	8	0.02	1.8	smooth	"
0.1182	0.1181	4	1	"	60	8½	0.02	1.7	"	"
0.1182	0.1184	4	2	125	66	24	0.02	2.0	"	"
0.1182	0.1186	2	1	125	60	8	0.02	1.8	"	"
0.1182	0.1180	2	1	125	50	"	0.02	2.0	"	metallic.
0.1182	0.1181	2	1	150	45	8	0.02	1.8	"	"
0.1182	0.1180	2	1	150	45	7½	0.02	1.8	"	"
0.1182	0.1181	2	1	200	"	"	0.02	"	"	"
0.0591	0.0590	2	1	150	45	24	0.02	1.9	"	metallic.
0.1182	0.1179	2	2	125	"	7½	0.02	1.7	rough	"
0.1182	0.1188	2	1	125	60	7	0.02	1.8	"	"
0.1182	0.1186	2	1	125	62	7	0.02	2.0	"	"
0.1182	0.1180	2	1	125	50	"	0.02	2.0	smooth	crystalline.
0.1182	0.1176	1	1	125	60	7¾	0.02	1.7	"	"
0.1434	0.1433	2	1	150	45	22	0.02	2.0	"	dark gray.
0.1434	0.1438	2	1	150	45	9¾	0.02	1.8	"	light gray.
0.1434	0.1438	2	1	150	45	18	0.02	1.8	"	"
0.1434	0.1434	2	1	150	45	24	0.02	1.8	"	rather dark.

## FROM SODIUM SULPHATE SOLUTION, USING BASKET ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D. <sub>100</sub> . Ampere.	Voltage. Volts.	Character of the deposit.
0.1182	0.1187	2	1	125	6½	60	0.03	2.1	light gray, metallic.
0.1182	0.1171	2	1	125	6¾	55	0.03	2.0	dark, but adherent.
0.1182	0.1176	2	1	125	7	55	0.02	1.8	dark gray.
0.1434	0.1436	2	1	150	22	45	0.02	1.8	light and metallic.
0.1434	0.1436	2	1	150	20	45	0.02	1.8	good, but a little dark.
0.1434	0.1431	2	1	150	18	45	0.02	1.8	light gray.

## FROM SODIUM SULPHATE SOLUTION, USING GAUZE ELECTRODES.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Sodium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D. <sub>100</sub> . Ampere.	Voltage. Volts.	Character of the deposit.
0.1182	0.1181	2	1	200	24	45	0.03	2.0	light gray.
0.1434	0.1433	2	1	200	7	45	0.03	2.0	" " very metallic.
0.1434	0.1434	2	1	200	9¾	45	0.03	2.0	" " "
0.1434	0.1433	2	1	200	8¾	45	0.03	2.0	" " "

## FROM POTASSIUM SULPHATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Potassium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D. <sub>100</sub> . Ampere.	Voltage. Volts.	Character of the deposit.
0.1434	0.1428	2	0.6	150	8	45	0.02	1.9	light gray.
0.1434	0.1436	2	0.6	150	9	50	0.02	1.9	" " very metallic.
0.1395	0.1400	2	1.0	250	9	45	0.025	1.9	" " "
0.1395	0.1392	2	1.0	150	6½	45	0.02	1.8	" " "
0.2790	0.2790	2	1.0	150	9	45	0.025	1.9	dark, but adherent.
0.1395*	0.1393	2	1.0	150	6	45	0.02	1.7	light gray.
0.0698*	0.0698	2	1.0	150	7	50	0.02	1.8	" " "

\* Basket anode.



## FROM POTASSIUM SULPHATE SOLUTION, USING GAUZE ELECTRODES.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Potassium sulphate. Gram.	Dilution. Cc.	Time. Hours.	Temperature. °C.	Current strength. Ampere.	Voltage. Volts.	Character of the deposit. light and adherent.
0.1395	0.1394	2	1.0	200	8	45	0.06	2	" "
0.1395	0.1394	2	1.0	200	8	45	0.04	2	" "
0.1395	0.1393	2	1.0	200	7½	50	0.05	2	dark "
0.1434	0.1435	2	0.6	200	9	50	0.03	2	light and metallic.
0.1434	0.1435	2	1.0	200	8	55	0.04	2	"
0.1434	0.1431	2	1.0	200	9	50	0.035	2	" metallic.
0.1434	0.1433	2	1.0	200	8¾	45	0.03	2	" "
0.1434	0.1430	2	1.0	200	..	45	0.03	2	" "

## FROM AMMONIUM SULPHATE SOLUTION, USING FLAT SPIRAL ANODE.

Bismuth taken. Gram.	Bismuth found. Gram.	Sulphuric acid. Cc.	Ammonium sulphate. Grams.	Dilution. Cc.	Time. Hours.	Temperature. °C.	N.D. 100. Ampere.	Voltage. Volts.	Anodes. discolored	Character of the deposit. light gray and metallic.
0.1182	0.1186	2	1	125	7	63	0.02	1.8	discolored	" "
0.1182	0.1186	2	3	125	8	60	0.02	1.7	"	" "
0.1182	0.1186	2	2	125	30	..	0.02	..	"	" "
0.1182	0.1174	2	2	125	7	..	0.02	..	"	" "
0.1182	0.1186	2	1	125	8	60	0.02	1.8 not	"	" crystalline.
0.1182	0.1180	2	1	125	8	60	0.02	1.8	discolored	" "
0.1182	0.1189	2	1	125	9	60	0.02	1.8 not	"	" "
0.1182	0.1179	2	1	125	8½	55	0.02	1.8	"	light gray.

to 0.15 ampere to bring down the last traces of bismuth. When gauze electrodes are used, such as were described in an earlier part of this paper, a current strength of 0.04 ampere should be used.

Heat is absolutely essential in order to obtain light, metallic deposits. If, however, the electrolysis be conducted two and a half to three hours at  $45^{\circ}\text{C}$ ., during which time most of the metal will have been deposited, it may safely be run over night in the cold. This procedure may, in some cases, be more convenient than conducting the electrolysis eight hours during the day at  $45^{\circ}\text{C}$ .

The end of the electrolysis is ascertained by raising the level of the liquid in the dish, or by testing a few drops of the solution for bismuth with ammonium sulphide.

When the metal has all been precipitated, the deposit is washed without interrupting the current. This is done by siphoning off the acid liquid, at the same time replacing it with hot distilled water. When the liquid in the dish is free from acid, the current is interrupted and the liquid poured from the dish. The deposit is washed with a little hot water and drained. It is then rinsed with a little absolute alcohol to remove the remaining water, this treatment being followed by a little ether. Finally the dish is gently warmed over a very small flame until complete evaporation of the ether, when it is desiccated, cooled and weighed.

With a good many deposits it was noticed that the alcohol tended to lift some of the deposited metal and float it away, thus involving loss. This was remedied by substituting for the alcohol a mixture of ether (2 parts) and alcohol (1 part). Treatment with this mixture is followed by anhydrous ether as usual.

When no dehydrating agents are used and the deposit is simply dried in the air by gently warming, an oxidation of the bismuth always takes place, giving high results.

The liquid should be maintained at a constant level during the electrolysis. If the level is raised, a dark border of loosely deposited bismuth forms around the dish, the depth of the liquid added. If the cover-glasses are close-fitting, scarcely any evaporation can take place, so that it is necessary to add but very little water during the electrolysis.

If the conditions as above stated be carefully followed, a good determination can always be obtained.

The problem of the electrolytic estimation of bismuth having been satisfactorily solved, attention was next given to its separation from other metals by the same means. The results of the experimentation in this direction are embodied in what follows.

#### SEPARATIONS.

(1) *Bismuth from Zinc.*—These metals can be separated with ease and precision electrolytically, from sulphuric acid solution. The bismuth comes down in a beautiful compact metallic form in every case free from zinc.

To 10 cc. of a nitric acid solution of bismuth containing 0.15 gram of bismuth and 1 cc. of nitric acid (sp. gr. 1.42) were added 2 cc. of sulphuric acid (sp. gr. 1.84), 0.6 gram of potassium sulphate and a quantity of zinc sulphate equivalent to 0.15 gram of zinc. The solution was then diluted with water to 150 cc. and electrolyzed with a current strength of 0.02 ampere and a voltage of 2.0. The solution was heated to 50° C. The deposition was complete in about eight hours. The same precautions previously observed as to the treatment of the deposited bismuth were of course followed here.

In the following table the results of four determinations are recorded.

#### RESULTS.

Bismuth taken.	Bismuth found.	Zinc.	Sulphuric acid.	Potass'm sulphate.	Dilution.	Time.	Temperature.	N.D. 100.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Cc.	Gram.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1433	0.1684	2	0.6	150	8½	50	0.025	2	basket.
0.1434	0.1430	0.1529	2	0.5	150	8	50	0.02	2	spiral.
0.1424	0.1428	0.1640	2	0.5	150	8½	50	0.025	2	basket.

(2) *Bismuth from Cadmium.*—The separation of bismuth from cadmium can also be accomplished with ease and accuracy. The conditions of the separation are very similar to those of bismuth from zinc. A quantity of cadmium oxide equivalent to 0.1500 gram of cadmium was dissolved in 2 cc. of concentrated sulphuric

acid (sp. gr. 1.84). To this solution were added 10 cc. of the bismuth solution containing 0.15 gram of bismuth and 1 cc. of concentrated nitric acid, 1 gram of potassium sulphate and the whole then diluted to 150 cc. Cadmium sulphate or nitrate may be used instead of the oxide. The solution was electrolyzed at a temperature of 50° C. and with a current strength of 0.025 ampere and 2 volts.

In all of the determinations recorded below the bismuth was deposited in light, metallic form, and was absolutely free from cadmium.

## RESULTS.

Bismuth taken.	Bismuth found.	Cadmium taken.	Potassium sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D. <sub>100</sub> .	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1395	0.1390	0.1500	1	2	150	8	50	0.025	2	basket.
0.1395	0.1400	0.1500	1	2	150	8	50	0.03	2	spiral.
0.1395	0.1400	0.1500	1	2	150	8	45	0.035	2	"
0.1395	0.1396	0.1500	1	2	150	8	45	0.03	2	basket.
0.1395	0.1398	0.1500	1	2	200	8	45	0.035	2	gauze.

(3) *Bismuth from Chromium*.—The next separation to receive study was that of bismuth from chromium. The chromium salt used in this case was chrome alum. The presence of chrome alum seems to exert a beneficial influence on the character of the deposit. It is interesting to note that during the electrolysis much of the chromium is oxidized into the condition of chromic acid, the color of the solution changing from green to yellow. On testing the solution, the presence of a large quantity of chromate can be shown. Especially is this the case when gauze electrodes are employed.

The electrolysis was carried out as follows: To a solution of bismuth containing 0.1500 gram of metal and 1 cc. of nitric acid (sp. gr. 1.42) were added, 0.5 gram of potassium sulphate, 2 cc. of sulphuric acid (sp. gr. 1.84) and a quantity of chrome alum equivalent to 0.1500 gram of chromium. This solution was diluted to 150 cc. with water and electrolyzed with a current strength of 0.025 ampere and a voltage of 2.0, the temperature

being maintained at 50° C. After eight hours the deposition was complete and the bismuth was found to be free from chromium.

## RESULTS.

Bismuth taken.	Bismuth found.	Chromium.	Potassium sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D. <sub>100</sub> .	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1430	0.1500	0.5	2	200	9	50	0.03	2	gauze.
0.1434	0.1428	0.1500	0.5	2	150	9	50	0.025	2	basket.
0.1434	0.1434	0.1500	0.5	2	200	8½	50	0.025	2	gauze.
0.1434	0.1428	0.1500	0.5	2	150	8½	50	0.02	2	basket.
0.1434	0.1430	0.1500	0.5	2	150	8½	50	0.02	2	spiral.
0.1434	0.1429	0.1500	0.5	2	150	9	50	0.025	2	"

(4) *Bismuth from Nickel*.—Nickel sulphate in quantity equivalent to 0.1500 gram of nickel, 0.5 gram of potassium sulphate, and 2 cc. of sulphuric acid (sp. gr. 1.84) were added to a solution of bismuth containing 0.1500 gram of metal and 1 cc. of nitric acid. This was diluted to 150 cc. with water and electrolyzed with a current of 0.025 ampere and 2 volts, the temperature being 45° C. The bismuth was completely deposited in nine hours and was free from nickel.

## RESULTS.

Bismuth taken.	Bismuth found.	Nickel taken.	Potassium sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D. <sub>100</sub> .	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1431	0.1500	0.5	2	150	9	40	0.025	2	spiral.
0.1434	0.1430	0.1500	0.5	2	150	9	40	0.025	2	basket.
0.1434	0.1434	0.1500	0.5	2	200	9	45	0.03	2	gauze.

(5) *Bismuth from Cobalt*.—The separation of bismuth from cobalt is easily effected. The conditions for their separation are identical with those given under bismuth from nickel. The salt of cobalt used in the following determinations was cobalt sulphate. The deposited bismuth was metallic in appearance and in every case free from cobalt.

## RESULTS.

Bismuth taken.	Bismuth found.	Cobalt taken.	Potass'm sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D. <sub>100</sub> .	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1429	0.1500	0.5	2	150	8¾	45	0.025	2	basket.
0.1434	0.1435	0.1500	0.5	2	150	8½	45	0.025	2	spiral.
0.1434	0.1430	0.1500	0.5	2	200	8½	45	0.03	2	gauze.

(6) *Bismuth from Manganese*.—Experiment showed that by this method the separation of bismuth from manganese could be effected without difficulty. The salt of manganese used in this case was manganous sulphate. The following mode of procedure was found to be the best: To a bismuth solution containing 0.1500 gram of metal and 1 cc. of nitric acid (sp. gr. 1.42) add 3 cc. of sulphuric acid (sp. gr. 1.84), 0.5 gram of potassium sulphate and a quantity of manganous sulphate equivalent to 0.1500 gram of manganese. Dilute this solution to 150 cc. with water and electrolyze with a current of 0.025 ampere and 2 volts, keeping the temperature at 45° C. The bismuth will be deposited in nine hours in beautiful form free from manganese.

At first the solution assumes a dark red color due to the oxidation of some of the manganese to permanganate. After an hour or two the color begins gradually to fade away and the solution again becomes colorless. A considerable quantity of hydrated oxide of manganese deposits on the anode during the electrolysis. This deposit was always examined for bismuth but in no case was it found to contain any of this metal.

## RESULTS.

Bismuth taken.	Bismuth found.	Manganese taken.	Potass'm sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D. <sub>100</sub> .	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1438	0.1500	0.5	3	150	23	45	0.025	1.9	spiral.
0.1434	0.1430	0.1500	0.5	3	150	9	45	0.025	2	"
0.1434	0.1435	0.1500	0.5	3	150	9	45	0.025	2	basket.
0.1395	0.1391	0.1500	0.5	3	150	9	45	0.035	2	gauze.

(7) *Bismuth from Uranium.*—Bismuth may be separated from this metal as follows: To a bismuth solution containing 0.1500 gram of bismuth and 1 cc. of nitric acid (sp. gr. 1.42) add 1 gram of potassium sulphate, 2 cc. of sulphuric acid (sp. gr. 1.84) and uranium sulphate equivalent to 0.10 gram of uranium. Dilute this solution to 150 cc. with water and electrolyze with a current strength of 0.025 ampere and a voltage of 2, maintaining the temperature at 45° C. The deposition is complete in eight hours and the deposited bismuth free from uranium.

## RESULTS.

Bismuth taken.	Bismuth found	Uranium taken.	Potassium sulphate.	Sulphuric acid.	Dilution.	Time.	Temperature.	N.D.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere	Volts.	
0.1395	0.1394	0.1000	1	2	150		45	0.025	2.1	spiral.
0.1395	0.1395	0.1000	1	2	150	8	45	0.03	0.2	basket.
0.1395	0.1399	0.1000	1	2	200	8	45	0.04	0.2	gauze.

(8) *Bismuth from Iron.*—The deposition of bismuth from solutions containing iron is attended with considerable difficulty. Both ferrous and ferric salts were experimented with. The iron present in the solution seems to exert an influence on the bismuth, tending to hold it in solution and prevent its deposition. Especially is this true when the salt used is a ferric salt. This tendency of bismuth to be held in solution is shown even in a more marked degree when the solution contains besides ferric alum an equal quantity of chrome alum. When this is the case, a current of 0.10 ampere will often not cause the slightest precipitation of bismuth. It was thought that this behavior of bismuth could be taken advantage of to separate other metals from it. It was hoped that the bismuth would be held back by the iron and chrome alums and such metals as mercury, copper and silver be deposited from the solution. These hopes were not realized. As soon as another metal is introduced, the condition of affairs is changed, and both the metal and the bismuth are precipitated. Deposits of silver, however, were obtained containing but very little co-

deposited bismuth. Further investigation in this direction might lead to some very interesting and valuable results.

The best conditions for the separation of bismuth from iron were found to be as follows: To the bismuth solution containing 0.15 gram of bismuth and 1 cc. of concentrated nitric acid, add 2 cc. of sulphuric acid (sp. gr. 1.84), 0.5 gram of potassium sulphate and a quantity of ferrous sulphate or ammonium ferric alum equivalent to 0.15 gram of iron. Dilute this solution to 150 cc. and electrolyze at a temperature of 45° C. If a ferrous salt is used, the current strength should be 0.03 ampere, but if a ferric salt is in solution a higher current strength should be employed, 0.05 ampere, the voltage in both cases being 2.0. In eight hours the deposition will be complete. The precipitated bismuth will contain no iron.

In several cases the separation was made in the presence of urea nitrate, but its addition was of no advantage. The same can be said for manganese sulphate, which was also added.

## RESULTS.

Bismuth taken.	Bismuth found.	Iron taken.	Urea nitrate.	Potassium sulphate.	Dilution.	Sulphuric acid.	Time.	Temperature.	N.D. 100.	Voltage.	Style of anode.
Gram.	Gram.	Gram.	Gram.	Gram.	Cc.	Cc.	Hours.	°C.	Ampere.	Volts.	
0.1434	0.1429	0.1500 <sup>2</sup>	...	0.5	150	2	8½	50	0.025	1.5	spiral.
.....	0.1431	0.1500 <sup>1</sup>	...	0.6	150	2	7½	45	0.03	2	"
.....	0.1435	0.1500 <sup>1</sup>	...	0.5	150	2	24	45	0.03	2	"
.....	0.1430	0.1500 <sup>1</sup>	...	0.5	150	2	24	45	0.03	1.7	basket.
0.1395	0.1394	0.1500 <sup>1</sup>	0.5	0.2	150	2	8	45	0.035	2	"
.....	0.1400	0.1500 <sup>1</sup>	0.5	0.2	150	2	8	50	0.035	2	spiral.
.....	0.1393	0.1500 <sup>1</sup>	0.5	0.2	200	2	8	45	0.05	2	gauze.
.....	0.1397	0.1500 <sup>2</sup>	...	0.5	150	2	9	45	0.07	2	spiral.
.....	0.1395	0.1500 <sup>2</sup>	...	0.1	150	2	9	45	0.06	2	"
.....	0.1394	0.1500 <sup>2</sup>	...	0.1	200	2	8	45	0.06	2	gauze.
.....	0.1395	0.1500 <sup>2</sup>	3.0	0.5	150	2	9	45	0.035	2	spiral.

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<sup>1</sup> Ferrous sulphate.

<sup>2</sup> Ferric ammonium sulphate.