

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]
**THE ELECTROLYTIC DETERMINATION OF TIN WITH THE USE
 OF A ROTATING ANODE.¹**

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Received January 25, 1907.

Tin has been the subject of considerable study in the way of determining it electrolytically². Exner³, working in this Laboratory, was the first to use the rotating anode in the electroanalysis of tin salts. From an oxalate electrolyte he precipitated as much as 0.5 gram of metal in thirteen minutes, using a current of $N. D_{100} = 5$ amperes and 5 volts.

As the rotating anode had never been applied in the deposition of this metal from an ammonium sulphide electrolyte the present investigation was undertaken.

Stannic chloride was the salt used. The ammonium sulphide had the specific gravity 0.985. The deposits were made in a platinum dish, using the form of anode described by Exner. Usually the ammonium sulphide was measured from a burette into the dish, and into this was allowed to flow the tin salt solution from a pipette. Sufficient water was added to make the volume equal 100 cc. Generally hot water was added. After covering the dish, the anode was rotated and the current passed. Sulphur invariably separated on the anode. It remained perfectly adherent. With a stationary anode, sulphur falls off and adheres to the metal deposit. The tin deposits were washed in the usual manner, *viz*: with warm water, alcohol and ether. They were dried by the heat of the hand and gentle blowing.

In the early trials stannous ammonium chloride was used. The results were as follows:

Table I.

No.	Sulphide.	Current amperes.	Volts.	Time, mins.	Tin present grams.	Tin found grams.
1	An excess	5.4	7	10	0.1357	0.1052
2	An excess	4	7.5	20	0.1357	0.1350
3	An excess	4	7.5	20	0.1357	0.1354
4	7 c.c.	4.5	8	25	0.1357	0.1358
5	7 c.c.	4 -3	8-7	22	0.1357	0.1357
6	14 c.c.	5.4-3	7-5.5	25	0.2714	0.2717
7	7 c.c.	5 -3	8-7	15	0.1357	0.1257

In numbers 1, 2, 4 and 7 the deposits resembled polished silver and remained perfectly bright even when rinsed with ammonium sulphide. Numbers 3 and 5 were rather dark colored for some unknown reason. In number 6 the acid of the tin solution was neutralized with a little am-

¹ From the author's thesis for Ph. D., 1906.

² Z. anal. Chem. 19, 13; Chem. News, 42, 291; Ber. 14, 1622; Z. Elektrochem. 2, 418 Smith's Elektrochemical Analysis, p. 113.

³ This Journal, 25, 896.

monium hydroxide and the precipitate then dissolved in ammonium sulphide. The solution from this and also those from numbers 2, 3, 4, 5 and 7 showed no trace of tin sulphide when acidified with hydrochloric acid, hence it is evident that over 0.13 gram of tin can be precipitated from an ammonium sulphide solution in 20 minutes and over 0.25 gram in 25 minutes.

A solution of stannic chloride was next electrolyzed with the following results; care being taken to vary the amount of sulphide and also the current:

Table II.

No.	Sulphide.	Current amperes	Volts.	Time, mins.	Tin present grams.	Tin found grams.
1	20 c.c.	5	8-7	20	0.1946	0.1932
2	20 c.c.	6	8.5	25	0.1946	0.1943
3	20 c.c.	11-8	11	15	0.1946	0.1944
4	15 c.c.	5.5	9	20	0.1946	0.1949
5	10 c.c.	5	9	20	0.1946	0.1946
6	8 c.c.	5	11	15	0.1946	0.1943

All the deposits were slightly crystalline but perfectly adherent. The solution from numbers 2, 3, 4 and 5 gave no test for tin. The best conditions for 0.2 gram of metal are 15-20 cc. of sulphide and a current of 5.5 amperes and 9 volts.

The deposits continued beautifully crystalline and perfectly adherent with 0.4 gram of metal. It was discovered that the speed of rotation of the anode had little or no effect on the character of the tin deposit.

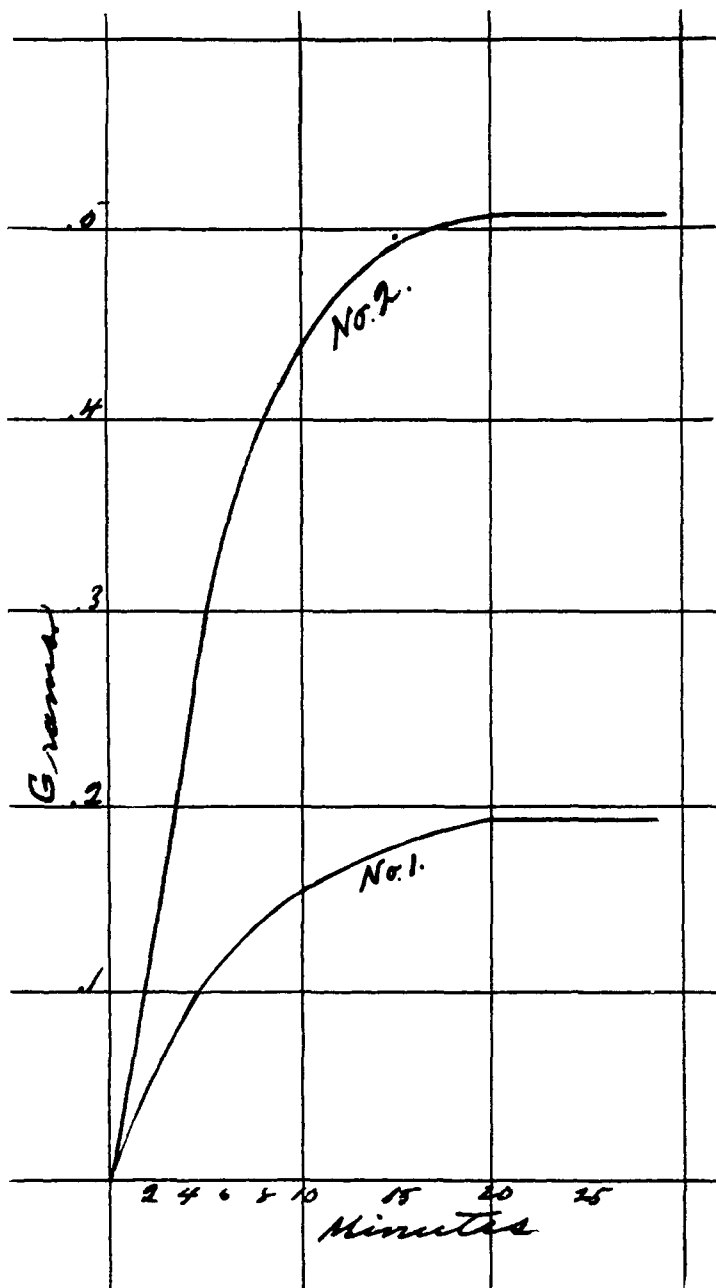
To obtain a time curve, a tin solution of about the same strength as that used to get the results in Table II was employed. The rate of deposition of metal was then carefully determined and Curve No. 1 drawn:

Table III.

No.	Sulphide in c.c.	Current amperes.	Volts.	Time, mins.	Tin found grams.
1	14	5	10	20	0.1935
2	14	5	10	25	0.1936
3	14	5	10	18	0.1924
4	14	5	10	20	0.1938
5	14	5	10	20	0.1939
6	14	5	10	20	0.1934
7	14	5	10	1	0.0225
8	14	5	10	2	0.0450
9	14	5	10	3	0.0707
10	14	5	10	4	0.0928
11	14	5	10	5	0.1083
12	14	5	10	10	0.1564
13	14	5	10	15	0.1840
14	14	5	10	20	0.1937

All the deposits weighing 0.1840 gram or less were bright, silver-white

in color, while they were finely crystalline when this amount was exceeded.



RATE OF DEPOSITION OF TIN.

The curve shows that the rate of precipitation is almost constant for the first five minutes, and then begins to decrease more and more rapidly. The rate of deposition is not as rapid in the first few minutes as has been noticed with other metals, but this can easily be accounted for by the fact that the electrolyte was not first heated.

Another series of analyses were made with a larger quantity of metal. The rate of precipitation was also determined and the curve (No. 2) drawn.

Table IV.

No.	Sulphide in c.c	Current amperes.	Volts.	Time, mins.	Tin found grams.
1	25	5	7.5	30	0.5069
2	25	5	8	30	0.5067
3	20	5	9	30	0.5070
4	20	5	9	20	0.5067
5	20	5	9	20	0.5064
6	20	5	9	20	0.5070
7	15	5	10	25	0.5069
8	20	5	9	1	0.0704
9	20	5	9	2	0.1276
10	20	5	9	3	0.1922
11	20	5	9	4	0.2475
12	20	5	9	5	0.2927
13	20	5	9	10	0.4796
14	20	5	9	15	0.7917
15	20	5	9	20	0.5070

In number 1 of this series, the water added was heated to about 40°, but in all the others it was heated to boiling and then added to the solution in the dish. In no case was the sulphide solution heated in the dish, as this seemed to affect the smoothness of the deposit. All the deposits weighing 0.5 gram were light grey in color and very finely crystalline. Those of smaller amounts were silver-white. The speed of rotation was 350-400 revolutions per minute. The time curve shows a very rapid precipitation for the first 10 minutes and then a rapid falling off during the deposition of the last traces.

When it was tried to deposit a gram or more of this metal, the results were too high and the deposits were spongy, although adherent.

Thinking that they might have occluded water, one of them was heated in an oven to a temperature of 150°-160° for an hour, but the loss in weight was practically nothing. This occurrence suggested that possibly some of the crystalline deposits of lower weight might have occluded something. To determine whether this was the case, a number of determinations were made, starting with a small quantity of metal which gave a bright, smooth silver-white deposit, and doubling the quantity each time, using the same pipette in measuring out the solution.

Table V.

No.	Sulphide in c.c.	Current amperes.	Volts.	Time,mins.	Tin present grams.	Tin found grams.
1	15	5	11	25	0.2038
2	20	5	9	25	0.4076	0.4077
3	20	5	9	25	0.6114	0.6118
4	21	5	9	25	0.8152	0.8152
5	25	5	9	25	1.0190	1.0235
6	25	5	9	25	1.0190	1.0216
7	25	5	8	30	1.0190	1.0232

The deposit in number 1 was bright and smooth, the others were crystalline but perfectly adherent. The solution gave no test for tin. Up to 0.8 gram, therefore, nothing was occluded, but above that they were always too heavy. Number 5 was washed with carbon bisulphide to remove sulphur, but the weight did not decrease.

From this brief study it may be concluded that tin can be determined in an ammonium sulphide electrolyte rapidly and accurately with the aid of a rotating anode. The deposition of metal is hastened by heating the electrolyte, while polysulphides retard it and their amount should therefore be made as small as possible.

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

ALKALIMETRIC METHOD FOR THE DETERMINATION OF TUNGSTEN IN STEEL.

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Received January 24, 1907.

Within the last ten years or more the greatly increasing use of tungsten steels under the name of "self-hardening" or "high speed" steel, and also the astonishing increase in the percentage of tungsten in the same, has been accompanied by the appearance in the literature of a number of new analytical methods for the determination of tungsten. Naturally the object sought has been the simplification of the method as far as possible without too great a sacrifice of accuracy as compared with the standard gravimetric method by precipitation as mercurous tungstate after the removal of carbon, silica, iron oxide, etc., by the several suitable but necessarily tedious operations involved. Strangely, most of these researches have been directed along gravimetric lines, and it may not be amiss to mention some of the more important ones without attempting a complete enumeration. Gravimetric methods have been described by Rodolfo Naumias¹, George Auchy², who suggests using a constant for the amount

¹ Stahl u. Eisen, 1891, II., 757.

² This Journal, 21, 240, 1899.