Some reduction products of selenic acid are formed during the electrolysis but these are insoluble and may be removed from the selenic acid solution by filtration.

The best efficiency yield, amounting to 87 per cent., was obtained with a low current density at the cathode, room temperature and a thin layer of lead selenate upon the cathode.

The best current yield, amounting to about 13 per cent., was obtained with a low current density, a hot solution (85°) and a large amount of lead selenate upon the cathode.

Only small amounts of selenic acid are formed from lead selenate in contact with the anode.

UNIVERSITY OF INDIANA, BLOOMINGTON,
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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

THE ELECTROLYTIC DETERMINATION OF NITRIC ACID.[1]

BY OWEN L. SHINN.

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In 1880 Lukow[2] found that nitric acid alone or in presence of sulphuric acid was not reduced to ammonia when electrolyzed between platinum electrodes. If, however, copper sulphate was added to the solution, reduction did take place, and if enough of the copper sulphate was added the reduction to ammonia was complete. He recognized the importance of an acid solution, as, in a solution which is alkaline, the change is oxidizing and ammonia is changed into nitric acid.

Lukow was satisfied with qualitative results and it remained for Vortmann[3] to develop the idea of making the operation a quantitative method for the determination of nitric acid. He also found that no ammonia was produced, even when the current was run continuously for several days, unless some metallic salt was added to the solution. He found copper sulphate to be the most satisfactory, but salts of other metals gave good results.

Easton[4] studied the conditions of this method with potassium nitrate and obtained good results. The method used was to add to a quantity of potassium nitrate an equal weight of copper sulphate, acidulate with sulphuric acid and electrolyze in a dish with a current of 0.2 to 3 ampere and a pressure of 3 to 8 volts. The time varied from one and one-half hours to seven hours, depending upon the current used. When the operation was complete the solution was poured off, the ammonia liberated

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[1] Read at the New Haven Meeting of the American Chemical Society.

[2] *Z. anal. Chem.*, **19**, 11.

[3] *Ber.*, **13**, 2798.

[4] THIS JOURNAL, **25**, 1042.

by sodium hydroxide and collected in standard sulphuric acid, the excess of which was titrated with standard alkali. His results varied from 13.32–13.77 per cent. of nitrogen; the mean of fifteen determinations was 13.59 per cent.

When the precipitation of metals by means of high current density and rotating anode was being studied in this laboratory, Ingham took up this problem and studied it along that line.[1] He made use of a suggestion made by Vortmann, which was not tried by Easton, *viz.*, to use standardized acid for acidulating and pure copper sulphate; then, instead of distilling the ammonia, to titrate the excess of acid in the solution which remained after the copper was all precipitated and the reduction was complete. He used a much stronger current than that used by Easton (4 to 5 amperes and 8 to 10 volts) and by agitating the liquid the reduction was complete in thirty minutes. One series of ten determinations, run in a single afternoon, gave results which varied from 13.79–13.94 per cent. of nitrogen, the mean value being 13.865 and the theoretical value 13.861.

Since Ingham published his paper several workers, trying this method, have complained of being unable to get as satisfactory results as were obtained by him and it was due to this fact that the study of the method was resumed by me.

The first experiments gave results which were rather unsatisfactory. The first series of twenty-five experiments, attempting to reproduce Ingham's work, gave results which varied from 12.71–13.92 per cent. of nitrogen with a mean of 13.55. Or rejecting two experiments which gave results below 13 per cent. the variation was from 13.11–13.92 with a mean of 13.65. Of these twenty-five determinations but eight gave results which were within 0.15 of the theoretical value.

The next series of twenty-five determinations gave results which varied from 13.20–13.87 with a mean of 13.65. In this series conditions varied in reference to the quantity of sulphuric acid, size of anode, distance between electrodes, quantity of copper sulphate, time of operation and current density, always using 4 amperes or over. The closeness with which these results agree with those of the last series would indicate that these changes have little influence.

The thought suggested itself that intermediate reduction products were formed, such as the volatile lower oxides of nitrogen or hydroxylamine. Several experiments, in which small quantities of alcohol were used with the idea of arresting the formation of these oxides, were nonproductive; the alcohol was oxidized and the nitric acid unaffected. The gases formed during the electrolysis were examined for nitrogen oxides and they were proven to be absent. The solution after electrolysis was

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[1] THIS JOURNAL, 26, 1251.

tested for hydroxylamine and this was proven to be absent. A further test for oxidizing intermediate products, such as the oxides of nitrogen or hydrogen peroxide, was made by adding alcohol after electrolysis and allowing to stand for an hour, allowing a second to stand for an hour and a half before titrating. Results gave 13.69–13.66 per cent. of nitrogen. Unreduced nitric acid was later proven to be in some of the solutions giving low results.

In a series of time experiments it was noted that the greater part of the reduction took place in the first fifteen minutes. Patton[1] gives results which indicate a similar condition. These facts in conjunction with the observation of Easton[2] that the material from which the cathode was made had no influence but that reduction did take place when a copper anode was used, led to the suggestion that if precautions be taken to keep copper in the solution the reduction might be made complete. The copper sulphate solution used contained about 0.25 gram of copper in 25 cc. This quantity of copper would be precipitated in ten minutes and even when double that quantity was used fifteen minutes were sufficient to complete the precipitation. If then, as it would appear, the reduction takes place at the same time that the copper is precipitated, if copper is kept in the solution by the addition of subsequent quantities of copper sulphate solution the reduction of the last traces of the nitric acid will take place. That this supposition was correct is shown by the results obtained in the next series of six determinations. In this series three additions of copper sulphate (25 cc. each) were made at fifteen-minute intervals. The results were as follows:

13.87, 13.81, 13.85, 13.95, 13.90, 13.82. Mean, 13.833 per cent. of nitrogen.

The next question was: Is that quantity of copper sulphate necessary? A series was then run adding three instalments of copper sulphate solution of 20, 15 and 15 cc. and 25, 12.5 and 12.5 cc. at fifteen-minute intervals. The following results were obtained:

13.79, 13.79, 13.76, 13.81, 13.82. Mean, 13.794 per cent. of nitrogen.

All of the determinations up to this time were made by titration. A series was then carried on in which the solution, after reduction, was distilled with sodium hydroxide and the ammonia evolved collected in standard acid, the excess of which was then titrated with standard ammonia. The conditions of the reduction were the same as in the titration experiments and the results were:

13.81, 13.81, 13.81, 13.75, 13.86. Mean, 13.808 per cent. of nitrogen.

As the rapidity of the precipitation of the copper is largely dependent upon the speed at which the anode rotates, it would seem as though

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[1] *Proc. Elec. Chem. Soc.*, 1908.

[2] *Loc. cit.*

this would have a corresponding influence upon the completeness of the reduction. That this is true the following series of results will show. Here twenty-five cubic centimeters of copper sulphate were added at the beginning of the experiment and no second addition made, otherwise the conditions were the same as those above with the exception of the speed at which the anode rotated:

Revolutions per minute.	Per cent. of nitrogen found.
130	13.86
130	13.81
130	13.81
150	13.73
150	13.70
300	13.62
500	13.60
750	13.49

These experiments would seem to prove that the reduction of the nitric acid takes place simultaneously with the precipitation of the copper and the slower the precipitation the more complete the reduction. Trials were then made to see if one addition of copper sulphate would give complete reduction if precautions were taken to keep the copper in solution for some time. This was done by retarding the rotation of the anode. With speed of 120 revolutions per minute, the results were 13.81 and 13.78 per cent. of nitrogen, and with stationary anode 13.82 and 13.80 were obtained.

When the rotation is slow and a current of 4 to 5 amperes with a pressure of 8 to 10 volts is passed through the solution the copper is thrown out as a spongy non-adhering deposit but it does not affect the result, the only precaution being to prevent the oxidation of the deposit on the dish before washing, otherwise the acid solution will act upon it and the results will be high. The dilute sulphuric acid in the solution has no effect upon the metallic copper even when it is in the spongy condition.

The question now comes: What are satisfactory conditions? Easton has shown that by a low current and a long time, the reduction is complete. Ingham's results can be duplicated if the rotation of the anode be kept slow so as to prolong the precipitation of the copper. The voltage should be about ten with a current of from 4 to 5 amperes. This requires that too much acid be not present; 20 to 25 cc. of $N/5$ sulphuric acid is ample. The only advantage gained by rotating the anode is an adhering copper deposit. When this is obtained it is necessary to add a second and sometimes a third portion of copper sulphate or the reduction will not be complete.

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