

# The Electrochemical Oxidation of Ammonia

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The Electro-synthesis of Potassium Nitrate  
from Potassium Hydroxide and Ammonia  
with a Dissolved Copper Catalyst

on a Low-Carbon Steel  
Anode

WGTR

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Revision 1

Experiments Are Adapted from the Following Reference:

Traube, Wilhelm, and Biltz, Arthur. "Die Gewinnung von Nitriten und Nitraten durch Elektrolytische Oxidation des Ammoniaks bei Gegenwart von Kupferhydroxyd." *Berichte der Deutschen Chemischen Gesellschaft* Vol. 37 (1904): 3130-38. Print.

The pathway to nitrate from non-nitrate sources presents a certain allure to a chemist. Most anyone can find enough stump remover or cold packs to provide enough nitrate for lab purposes. However, these sources can dry up or move around, forcing one to improvise to keep one's lab properly stocked. In some areas of the world it's not possible to get the requisite materials in any quantity. Even for those with no lack of ready supply, the ability to convert an extremely common material into a very useful one evokes an excitement that can't be explained well to those who just don't "get it". To the avid explorer of chemistry, this excitement can provide the most compelling motivation of all.

In the spirit of this excitement, it was with interest that the experiments of Traube and Biltz were studied, as they claimed the ability to oxidize ammonia into nitrite and nitrate salts. The equipment and materials used were simple and readily available, and their efforts were met with high faradaic efficiency. Though the reference is dated, as is common with so many interesting but forgotten synthetic procedures; the chemistry behind it is still relevant to the amateur chemist today.

It is the intention of this preliminary document to detail the experimental conditions and results of a small-scale electrochemical ammonia oxidation. It isn't necessarily as well-polished as desired, but still serves as an initial effort towards an end goal, that is, an attempt to verify the results of Traube and Biltz, as well as to create a useful synthetic procedure for the synthesis of potassium nitrate.

Traube and Biltz focused the bulk of their work on the sodium salts. Their reported yields for sodium nitrite were as high as 90%, based on faradaic efficiency. Conversion from ammonia to sodium nitrate was as high as 74%, based on the same metric. Brief effort was expended on investigating the potassium salts, and their reported yield for the conversion to potassium nitrite was only about 60%. Even with lower reported yields, it is in the potassium salt that we are most interested.

Potassium nitrate has a unique property among other common potassium salts, in that it has comparatively low water solubility at low temperatures. As the solution temperature increases, however, its solubility increases dramatically. For this reason it's a fairly easy salt to purify by crystallization. It may also be possible to crystallize this salt out as it's formed in situ, since it's much less soluble than even potassium nitrite. It's also easier to keep dry than the corresponding sodium salt. For these reasons,

the current effort is focused on the potassium salt.

Solubilities of relevant potassium salts  
in mol K<sup>+</sup> ion/L near R.T.

KOH	21.6
K <sub>2</sub> CO <sub>3</sub>	16.2
KHCO <sub>3</sub>	6.73
KNO <sub>2</sub>	36.7
KNO <sub>3</sub>	3.13

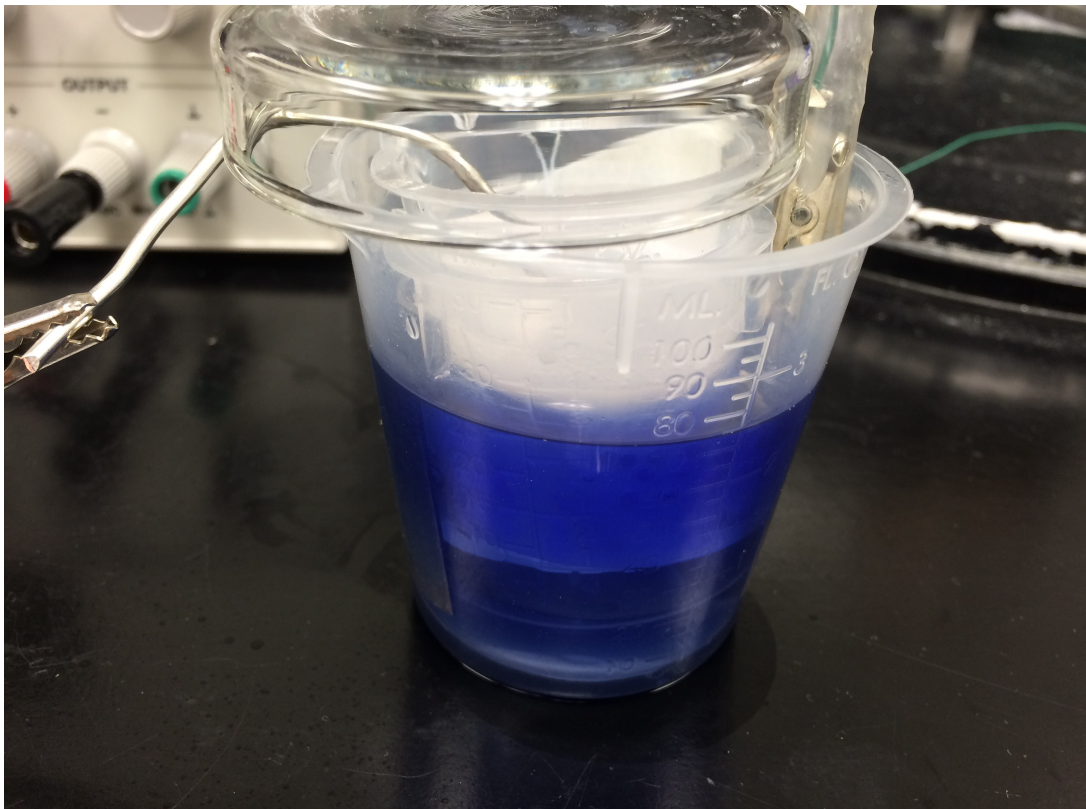
The starting materials were KOH (ACS Fisher), NH<sub>4</sub>OH (30% Fisher), basic copper carbonate (precipitated with NaHCO<sub>3</sub> from copper sulfate), and DI water. The anode is 1018 low carbon steel, and the cathode is tin-plated copper bus wire. Plastic cups of various sizes are used as containers and to provide partitions for divided cell electrolysis.

Two 30mL plastic beakers were used to divide the cathode from the anode compartment. The two cups were stacked together and then drilled through with about 50 holes (about 1/16" diameter ea.) around its circumference. After de-burring and cleaning the holes, the cups were separated, and then a single layer of Xerox copy paper was wrapped tightly around the inner cup. The inner cup was then pressed tightly into the outer cup, until the paper diaphragm was squeezed tightly in between the two. This structure provided support for the paper diaphragm, and kept it from disintegrating during the experiment.

A 100mL plastic beaker was used as the outer

container. Into this container the rounded steel anode (3.8cm x 10.0cm) was fitted to the inside diameter of the container.

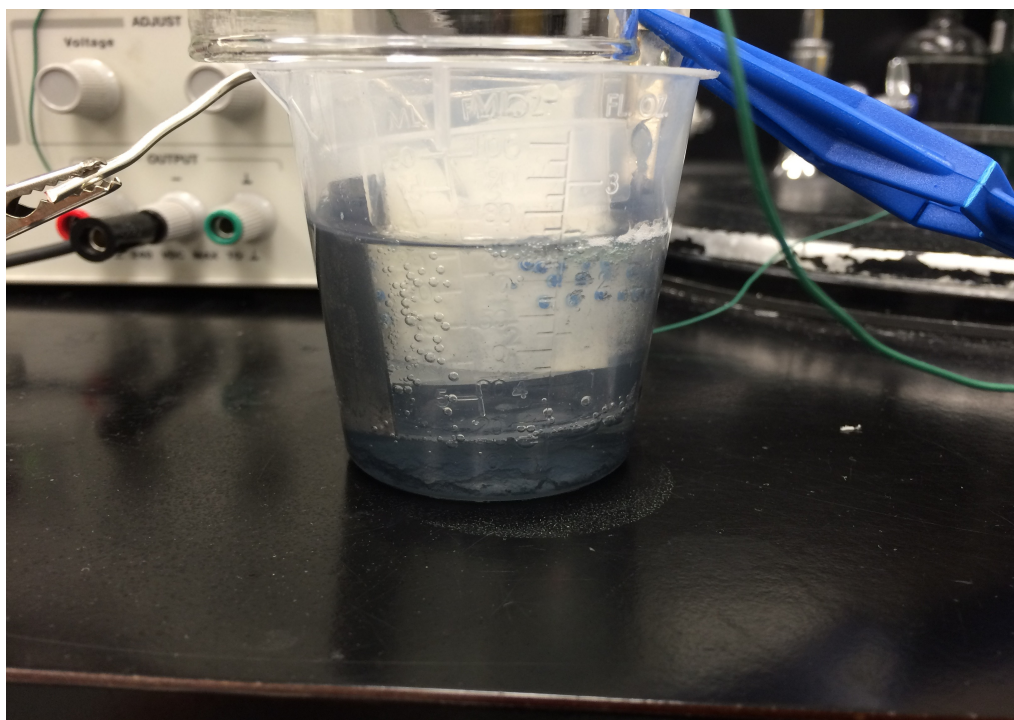
About 7g of KOH was dissolved into 80mL of DI water, and the solution divided between the anode and cathode compartments. Some extra solution was placed in the cathode compartment, so as to provide initial compensation for the ammonia that would be placed in the anode compartment. About 0.1g (was not measured exactly) of basic copper carbonate was added to 5mL of 30%  $\text{NH}_4\text{OH}$ , and the resulting bright blue solution mixed into the anode compartment.



Inner cup is cathode compartment, outer cup holds anolyte

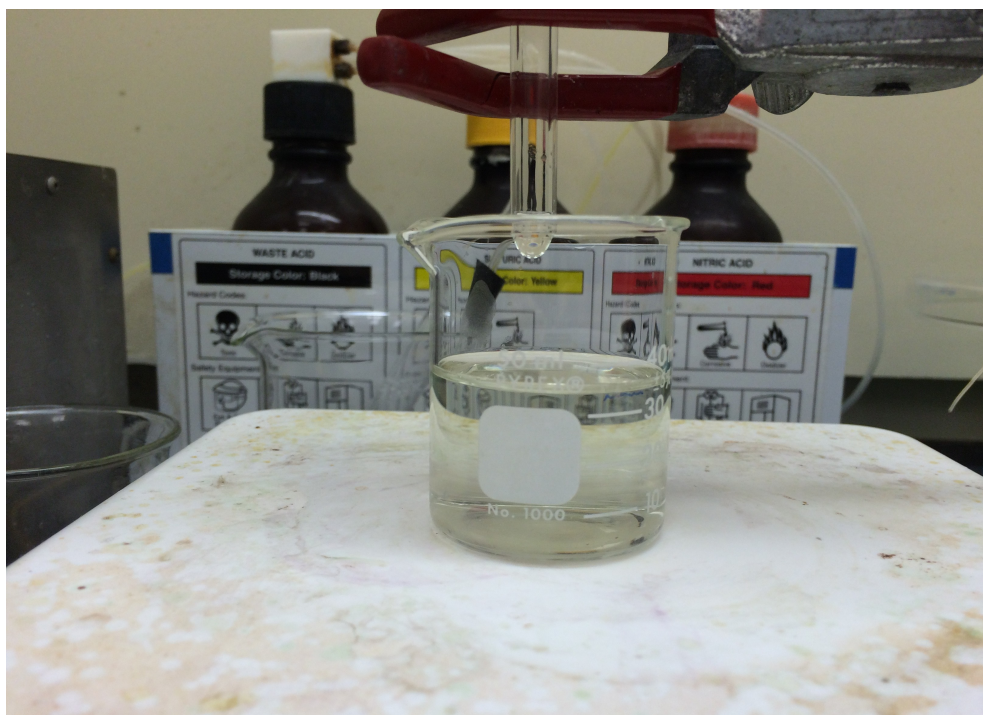
Electrolysis was performed for 16 hours at 0.300A. Cell voltage remained approximately 3.1-3.2V during the course of the experiment. Current density of the anode was between 0.008 to 0.004A/sq cm. The uncertainty is due to cell geometry, since both sides of the anode were exposed to the solution, and the anode current distribution was not uniform. Cathode current density was approximately 1.6A/sq cm. This probably gave rise to some power inefficiency, but shouldn't affect the faradaic yield if the diaphragm is sufficient to prevent significant migration of the nitrate to the cathode.

At the culmination of the 16 hour test, it was noted that all of the copper had precipitated out, leaving a clear,



faintly yellow, anolyte. Some small pieces of gelatinous

material were found floating; these may have originated from the diaphragm.



The resulting anolyte of about 40mL was filtered, treated with an additional 5.6g of KOH, and evaporated down to 20mL. The solution was cooled down to 0 deg. C, at which point a crop of crystals precipitated out. The solution was decanted off, and the crystals were treated with 20mL of boiling alcohol, and with small additions of hot water that were just enough to fully dissolve the precipitate. The solution was then allowed to cool slowly to room temperature, and a crop of crystals again precipitated. The solution was then placed in an ice bath to fully precipitate the salt. The precipitate was then washed with an additional 20mL of cold ethanol.

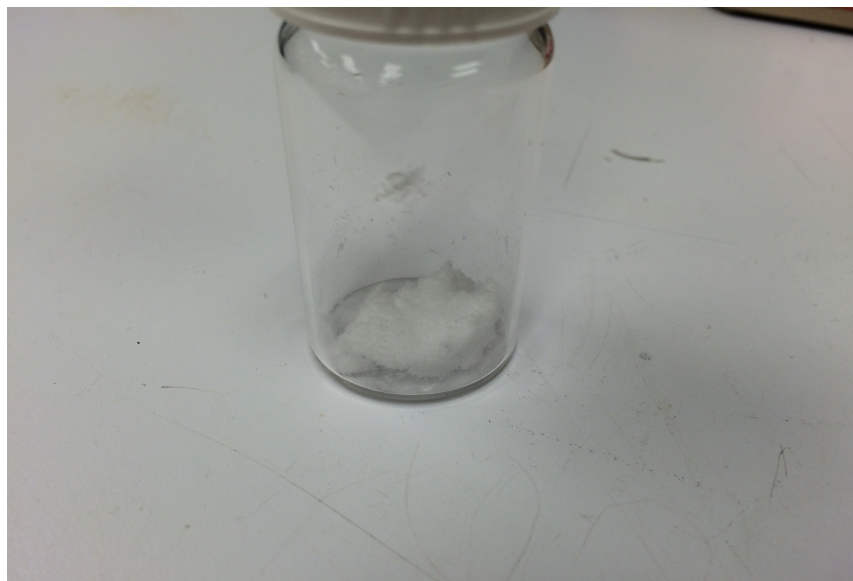
Filter paper was washed with DI water, dried in an



oven at 110 deg. C, and tared at 0.5302g. The precipitate was freed from the ethanol and placed on the filter paper, where it was dried in an oven at 102 deg. C. Some yellow coloration was noted on the filter paper after the product was fully dried.



Accounting for the weight of the paper, the amount of product obtained was 0.5131g.

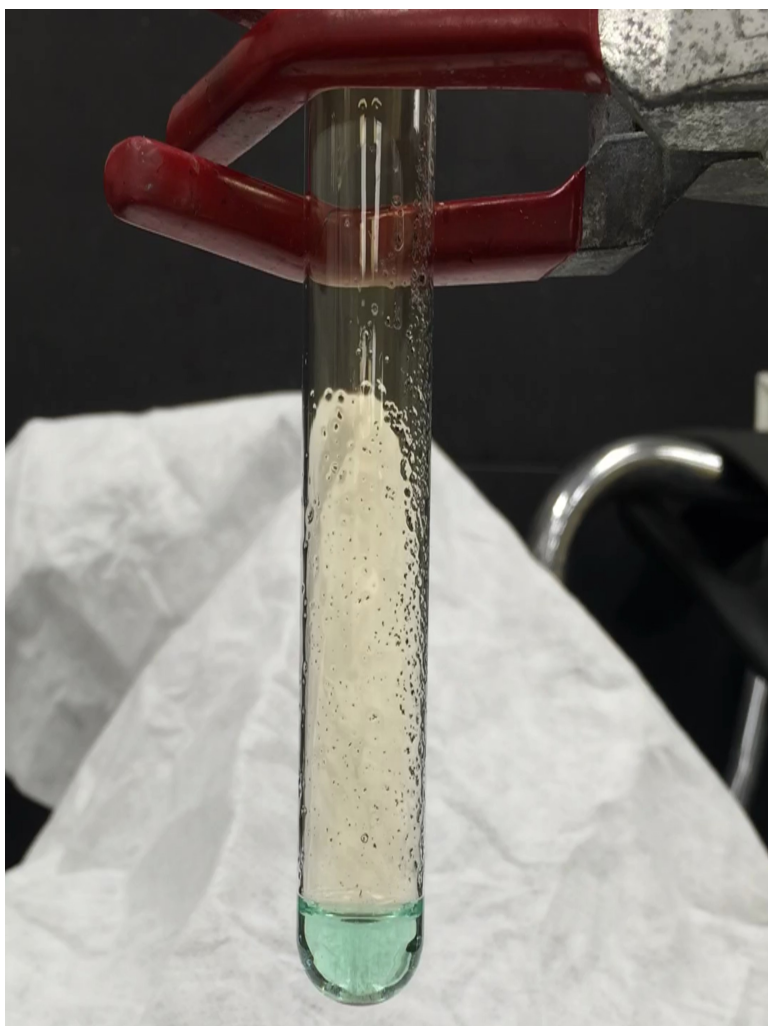


0.025g of the product was ground together coarsely with 0.0083g of balsa charcoal. The mixture was pressed onto a piece of paper with a metal spatula, and ignited. The sample's energetic response resembled sulfur-less black powder.



0.095g of the product was added to 1mL of DI water in a test tube. 0.20mL of  $H_2SO_4$  was added, and the solution mixed. No reaction was noted, therefore it was determined that the test for nitrite was negative. Immediately following, copper shavings were added to the solution, and gassing ensued from the copper. Gentle heating was

applied with a propane torch. Vigorous gassing occurred, and the reaction became self-heating. Over time, the solution turned green, and the head space filled with brown fumes. Therefore, it was determined that the test for nitrate was positive.



Based on the expected solubility differences of the various potassium salts, and the results from the preceding tests, it was determined that the product was potassium nitrate.

The yield of  $\text{KNO}_3$  was low in this experiment. For a

given current of 0.300A for 16 hours we have 17,280 Coulombs. Given the 8 units of charge needed for each unit of ammonia, this gives an expected yield of 2.3g of  $\text{KNO}_3$ , giving a total faradaic yield of about 22%. It's possible that a significant quantity of potassium ions were still present as nitrite. Concentrations of the electrolysis solutions may need to be increased. The diaphragm may not be performing its job very well, allowing nitrate to be reduced at the cathode to ammonia and other species. Since the nitrite salt is very soluble, it's likely that it still remained in solution during the crystallizations. It will be useful in the coming experiments to quantitatively test for nitrite with a permanganate titration. The cathode fluids should also be tested, to see how well the paper diaphragm is performing its function.

It's unknown what affect carbonate would've had on the results. It would be very useful to know if  $\text{K}_2\text{CO}_3$  could be used instead of  $\text{KOH}$ , both due to availability and air stability.