Production of Crystallized Ammonia Target Material for Nuclear Experimentation

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The making of solid ammonia as target material is a well documented and replicated process. However there is scope for improvement in terms of the quantity and quality of solid ammonia production. This paper provides an exposition of relevant existing knowledge, techniques, and details the improvements made for the process of making solid ammonia at the Solid Polarized Target Group at the University of Virginia, which have been demonstrated in terms of efficiency of both time and materials. Included are a manual for ammonia production as well as relevant technical drawings.

I. BACKGROUND AND MOTIVATION

A solid polarized target has the advantage over gaseous targets due to high nucleon density. Combined with high beam currents, solid polarized targets provide some of the highest luminosity experiments for the extraction of polarized target observables. Here we explore making glassy matrix based ammonia as well as crystallize ammonia. Crystallized ammonia is expected to be much more durable an may prove to be useful when exploring further ammonia fragment shapes with the goal of improving packing fraction. The density is also greater for the crystallized form.

A. About Ammonia

Ammonia is NH_3 that consists of one nitrogen and three hydrogen atoms. It is gaseous at room temperature and under atmospheric pressure the melting point is 195.45 K and the boiling point is 239.8 K. The ammonia molecule is shaped like a tetrahedron (an equilateral triangle based pyramid). The hydrogen atoms are located on the same plane.

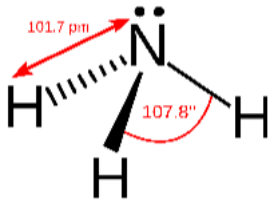

FIG. 1. Ammonia Molecule 2D representation

Ammonia is a colorless, diamagnetic pungent odor gas. It is a very aggressive chemical and corrodes many common metals and plastics. It is lighter than air. Due to it's high critical temperature[6] of 405.5 K, critical pressure[6] of 111.3 atm and critical density[6] of 225 kg/m^3 it is easily converted into a colorless, low viscosity liquid. The making of solid ammonia, as this paper will detail, is more tedious if it is to have the physical properties required to make good target material in a polycrystalline structure.

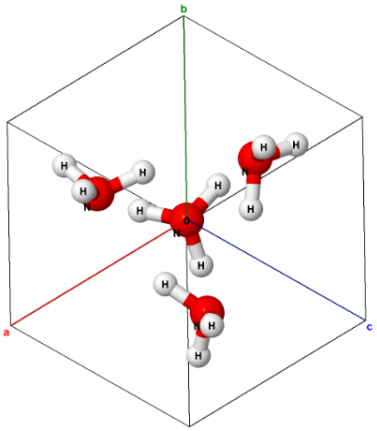

FIG. 2. Elementary cell of ammonia molecule

The ammonia single crystal has cubic symmetry with a space group of $P2_13$. The axis of symmetry is along the diagonals of the elementary cell. If the crystal is rotated 120° about this axis, the resulting position will be identical to the initial state.

ND_3 is similar, except the unit cell is smaller due to a larger dipole moment ($\mu_{NH_3} = 1.4712$ D[5]; $\mu_{ND_3} = 1.497$ D[4]. This can also be understood in terms of organic chemistry (bond lengths, electronegativity). Since deuterium has a higher mass than protium, the deuterium 1s electron will have a smaller orbital radius than the 1s electron orbiting the protium nucleus. The smaller orbital radius for the deuterium electron translates into a shorter and stronger ND bond length.

A shorter bond has less volume to spread the electron density (of the 1 electron contributed by H or D) over resulting in a higher electron density throughout the bond, and, consequently, more electron density at the Nitrogen end of the bond. Therefore, the shorter N-D bond will have more electron density around the Nitrogen end of

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the bond, than the longer N-H bond.

The net effect is that the shorter bond with deuterium increases the electron density at Nitrogen, e.g. deuterium is inductively more electron donating than protium towards Nitrogen.

B. Solid Ammonia as Target Material

Solid ammonia has one of the simplest molecular structures. The molecules are bound together by weak hydrogen bonds involving the lone pair of electrons, which with the three H atoms make up a rigid tetrahedron around the N atom. In the solid state, ammonia is an ideal material for the study of the dynamics of simple molecular crystals.[1]

Ammonia was chosen as the target material because it has the highest resistance to degradation of polarization by radiation damage.[15]NH_3 and [15]ND_3 (which is much more expensive) are used rather than [14]NH_3 because the lack of a polarized neutron in [15]N leads to a smaller correction and error on the spin asymmetry measurement.

Ammonia as a target material has a much greater dilution factor than, say, alcohol or butanol (13.5%). The dilution factor is the ratio of the number of polarizable nucleons to the total number of nucleons in the material. It can be expressed as follows:

$$f(x) = \frac{n_H \bar{\sigma}_H^T}{\Sigma_A n_A \bar{\sigma}_{N(A)}^T}$$

where f(x) is the dilution factor and the index T refers to total cross sections (including radiative effects). In this formula, n_A is the total number of nucleons (for the full target) in nuclei with atomic number A and $\sigma_{N(A)}$ the unpolarized cross section per nucleon on nucleus A.[3]

II. METHODOLOGY

As with most other materials, the most straightforward way to make solid ammonia is to liquify ammonia gas and then introduce it to a cold medium such as liquid nitrogen. Indeed, when removing the crystal we do not let the liquid ammonia go to waste.

Large amounts of liquid ammonia are solidified in a very short time relative to forming crystalline solid ammonia. However, the beads formed this way are extremely brittle, powdery and tend to have empty pockets due to the mixing and then vaporizing of liquid nitrogen bubbles.

This makes for uncertainty in the density of the target material and increases the chances of material being lost to vaporization during transfer.

In other processes in the past by groups in Germany and at UVA the more time consuming route has been taken as a result. In the German group's process the ammonia is first liquefied in a flask and then slowly frozen for a stable yield with high density. The flask is placed in an ethanol bath with liquid nitrogen being used for cooling. Argon is used so as to avoid condensation of oxygen or water among other impurities. After protecting the material by submerging it under liquid nitrogen and sieving it, this setup had a yield of 30g per 6h hour session or 5g/hour.[2]

Since chemical addition of radicals isn't possible, the ammonia solid ammonia has to be irradiated after production. Radicals especially should be kept separate from this solidification process because they would cause clustering during the freezing process thereby being unevenly distributed throughout the sample.

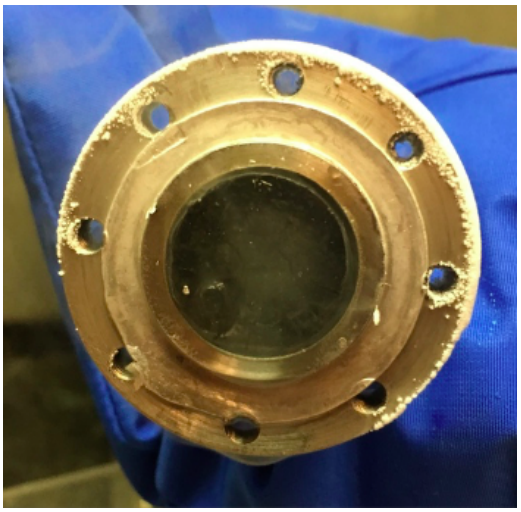

FIG. 3. Liquid NH_3 surrounding the solid ammonia being dropped into liq N_2.

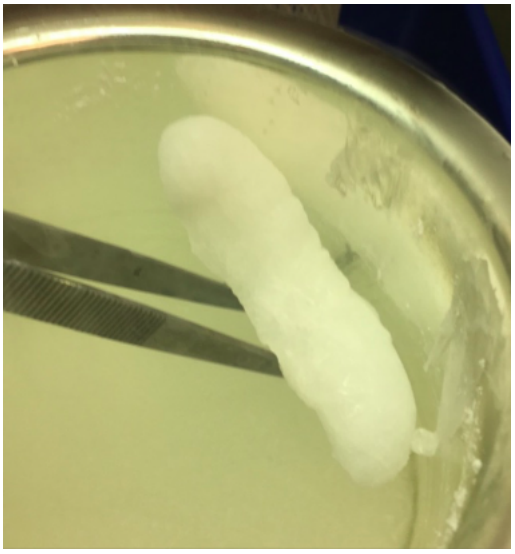

FIG. 4. Large amounts of solid ammonia by suddenly freezing liquid

FIG. 5. Brittle ammonia being lost to vaporization

FIG. 6. Lower yield from the old method

A. Crystallization of Ammonia

The quantities of ammonia claimed here can be easily verified:

- Capacity of each storage bottle: 30ml
- Density of solid ammonia: 817kg/m^3

This gives 24.5g/bottle of solid ammonia. Accounting for the granular nature of the material after crushing it through the sieves an approximate of 20g/bottle is helpful to check claims of quantity of solid ammonia (yield) for each session.

By the same logic at least 0.2 kg of solid ammonia was produced in the course of this project alone.

1. Setup and Material Production prior to Summer 2016

This method was used as a basis for improvement throughout the summer and fall semesters of 2016. The manual for this can be found in the appendix section

The method previous to the changes reflected in the manual's procedure had a yield of 8-10g per 1.5 hour session or 6.7g/hour.

This method is fairly reliable as long as all the instructions are followed to the letter and there is no human error in terms of maintaining pressure and liquid nitrogen levels in the appropriate parts of the apparatus.

2. Modifications and Improvements

The procedure listed in the manual above was written before many of the improvements detailed here, which more than doubled the rate of production to 20g per 1.5 hour session or 13.4g/hour simply by a trial-and-error change, informed by basic gas laws through which the initial flow pressure was increased from 3psi to 6psi. These durations do not count the 30-40 minutes of setup and removal of material which is highly variable due to unexpected leaks, freezing screws, jammed seals etc. This yield is already almost 3X higher than previous methods.

A newer cylinder was designed to maximize the production of solid ammonia, the designs for which can be found in the appendix section of this paper **??**. This cylinder has 6X the volume of the previous cylinder and can produce 6X the material by merely increasing the flow rate to 9psi, increasing the flow duration from 30 minutes to an hour, and the resulting cool down taking 3 hours total. The new cylinder is cumbersome to use due to a lack of an appropriately sized dewar in which to place it, which caused problems while testing it with the dry ice method detailed below 7.

Consider the following data:

- Ammonia melting point: 195.45 K
- Deuterated ammonia melting point: 199.15 K
- liquid nitrogen temperature: 63 - 77.2 K
- dry ice temperature: 194.7 K
- 200% ethanol freezing point: 159.2 K

It is clear then that the temperature gradient produced by using liquid nitrogen to freeze the ammonia was too steep. Unlike the German setup where platinum detectors were used to monitor the inside temperature and control it accordingly, the metal cylinder in use here prevents the measurement of the inside temperature. It can be calculated and plotted based on the pressure and by using gas laws, however, every trend was plotted slightly differently due to the variance in human error such as letting the liquid nitrogen level drop too low, accidentally

spilling it inside the insulation cup etc. It can be simply described qualitatively as a steep temperature gradient.

Attempts at using liquid nitrogen in the cooling process in conjunction with dry ice and ethanol invariably failed due to the liquid nitrogen freezing everything around it causing blocks of ice that were very hard to break through, especially due to the lack of any precise temperature control.

FIG. 7. Dry Ice and ethanol frozen solid due to surrounding liquid nitrogen

Dry ice presents an opportunity for a lower temperature gradient simply due to the smaller temperature difference. Dry ice, however, is manufactured in pellets presenting the choice between grinding it all down to a powder, thereby increasing the surface area and allowing for faster sublimation, or using the ethanol bath to regulate the temperature. The latter option suits the purposes of making a solid ammonia crystal.

The setup was simply that of immersing the cylinder into the dry ice and ethanol bath and then following the same procedure as the manual.

Tip: to make the dry ice last longer and to cool down the ethanol so as to not cause a temperature spike when used to replenish the evaporated ethanol use the setup in image 9.

3. Analysis of the Dry Ice method

From the outset due to the slow and gradual decline in pressure within the cylinder it was clear that the dry ice - ethanol bath method was providing a temperature gradient that was closer to ideal than that of any of the previous methods.

The cool down process took around 6 hours and due to the fact that the pressure had stopped dropping at -15psi as compared to the usual -29psi it was clear that

FIG. 8. Dry Ice and ethanol bath setup

FIG. 9. Dry ice with liq N_2 filled bottles + bottles of ethanol

there was more material in the cylinder than had ever been produced before in a single session.

Upon removing the solid from the cylinder it looked clear and transparent, leading to the assumption that it was a crystal. However, this turned out to be merely the liquid ammonia filling in the cracks in the solid to give it this appearance. Upon being submerged in the liquid nitrogen, the cracks were clear and no piece was large enough to meet the threshold to test a single continuous crystal structure. The assumption underlying the process of solidification was that the liquid ammonia pools together before starting to freeze. However, as evident from the picture II A 3 and the hollow structure, the solidification is happening by means of layering and condensation.

The yield was very good with 60-80 g being produced, or 13.4g/hour, which is again 3X as much as previ-

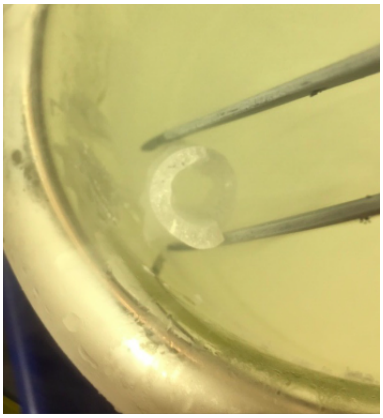

FIG. 10. Hollow structure

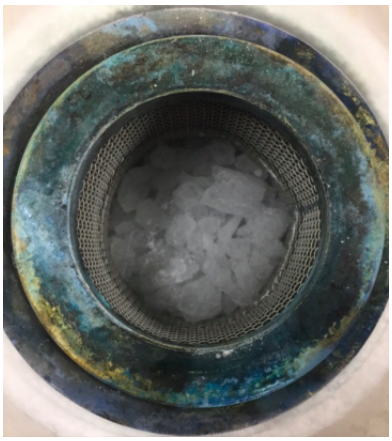

FIG. 11. yield before sieving

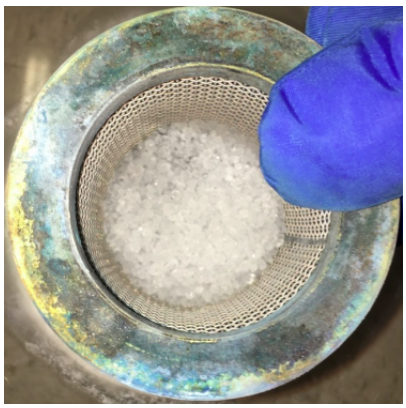

FIG. 12. A fraction of the yield after sieving; the rest had already been stored.

ous methods employed elsewhere, which is encouraging considering the improvements in the qualitative aspects. This yield was much harder, as observed while sieving, and therefore more dense than previous yields.

This phase diagram 13 has been referred through in all the optimization decisions for the production of solid ammonia. Here, A and B indicate the boiling and melting point at normal pressure whereas C marks the triple point of ammonia. D represents the triple point between the solids and liquid phase. The blue dot roughly marks the point at which our system exists during the solidification process. There is no initial pressure to final pressure change indicated due to the fact that the psi units used in the apparatus don't indicate significant difference when plotted in bar units.

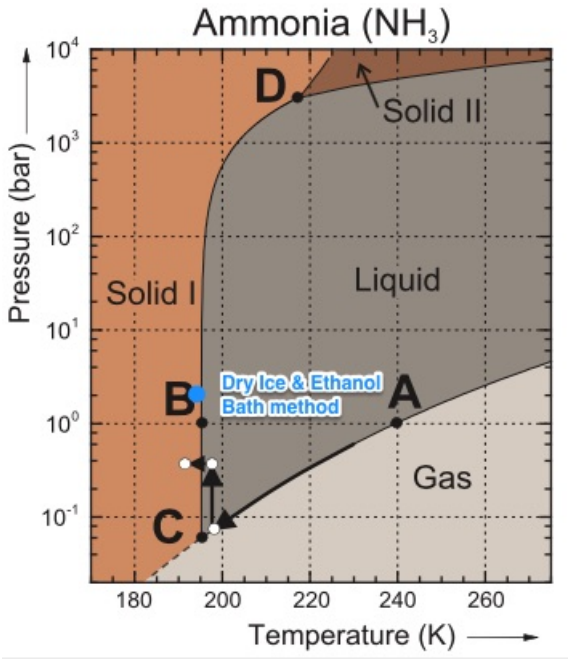

FIG. 13. Phase diagram of ammonia

III. CONCLUSIONS

The changes made to the gas flow and cooling duration parameters are optimal for solid ammonia production with the existing apparatus.

The yield using the dry ice - ethanol bath method indicates a higher degree of crystallization than has been produced before and suggests that the correct approach is being taken towards producing a crystal.

As seen in the phase diagram 13 the temperature needs to be gradually further decreased by means of liquid nitrogen so as to move away from the solid/liquid phase boundary. This can be accomplished by tubes or any variety of means.

IV. FURTHER STEPS

The rest of the process following from irradiating the crystal can proceed once a crystal that meets the qualitative thresholds for size and transparency has been produced.

The solid ammonia samples spread throughout the storage dewars needs to be consolidated carefully (minimizing loss in transfer) so as to ascertain the exact quantity produced so far and to make eventual usage of the material more convenient.

Most importantly, doing a long ammonia production session that will yield one or more solid ammonia crystals.

V. REFERENCES

[1] A. W. Hewat & C. Riekel, *The Crystal Structure of Deuteroammonia between 2 and 180 K by Neutron Powder Profile Refinement*, Feb 1979.
[2] Alexander Berlin, *Polarized Solid Ammonia Targets at the COMPASS Experiment at CERN*, September 2015.
[3] R. Windmolders, An Introduction to the Evaluation of Spin Structure Functions from Experimental Data, November 2013
[4] D. di Lonardo and A. Trombetti, 1981, Chem. Phys. Lett. 84, 327
[5] M. Takami, H. Jones, and T. Oka, The Journal of Chemical Physics 70, 3557 (1979)
[6] AirLiquide, *Gas Encyclopedia/Ammonia*, Accessed June 2016 at https://encyclopedia.airliquide.com/ammonia

VI. APPENDIX

The SolidWorks drawings that were made to produce the solid ammonia are shown.

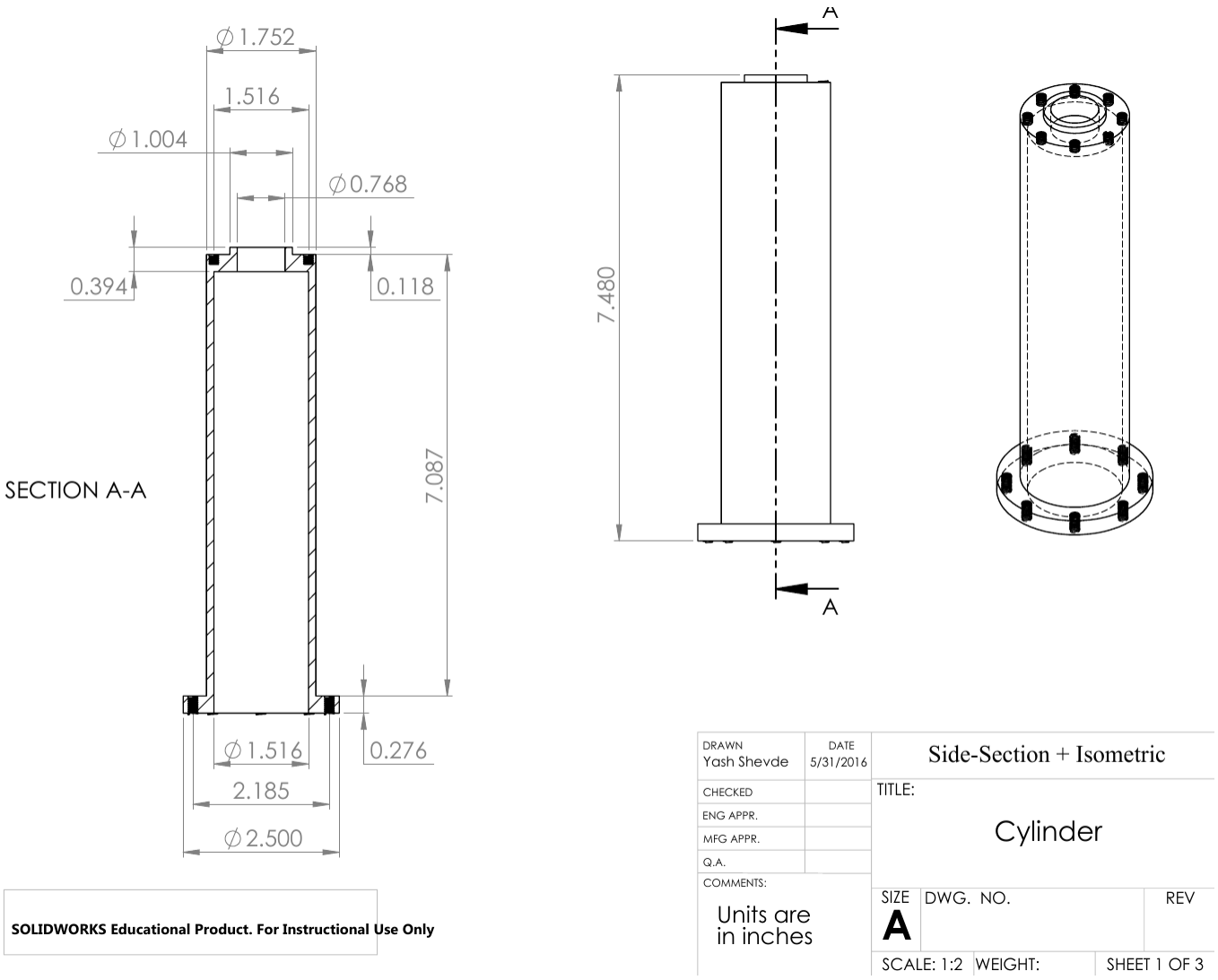

FIG. 14. The drawing of the cylinder for solid ammonia making.

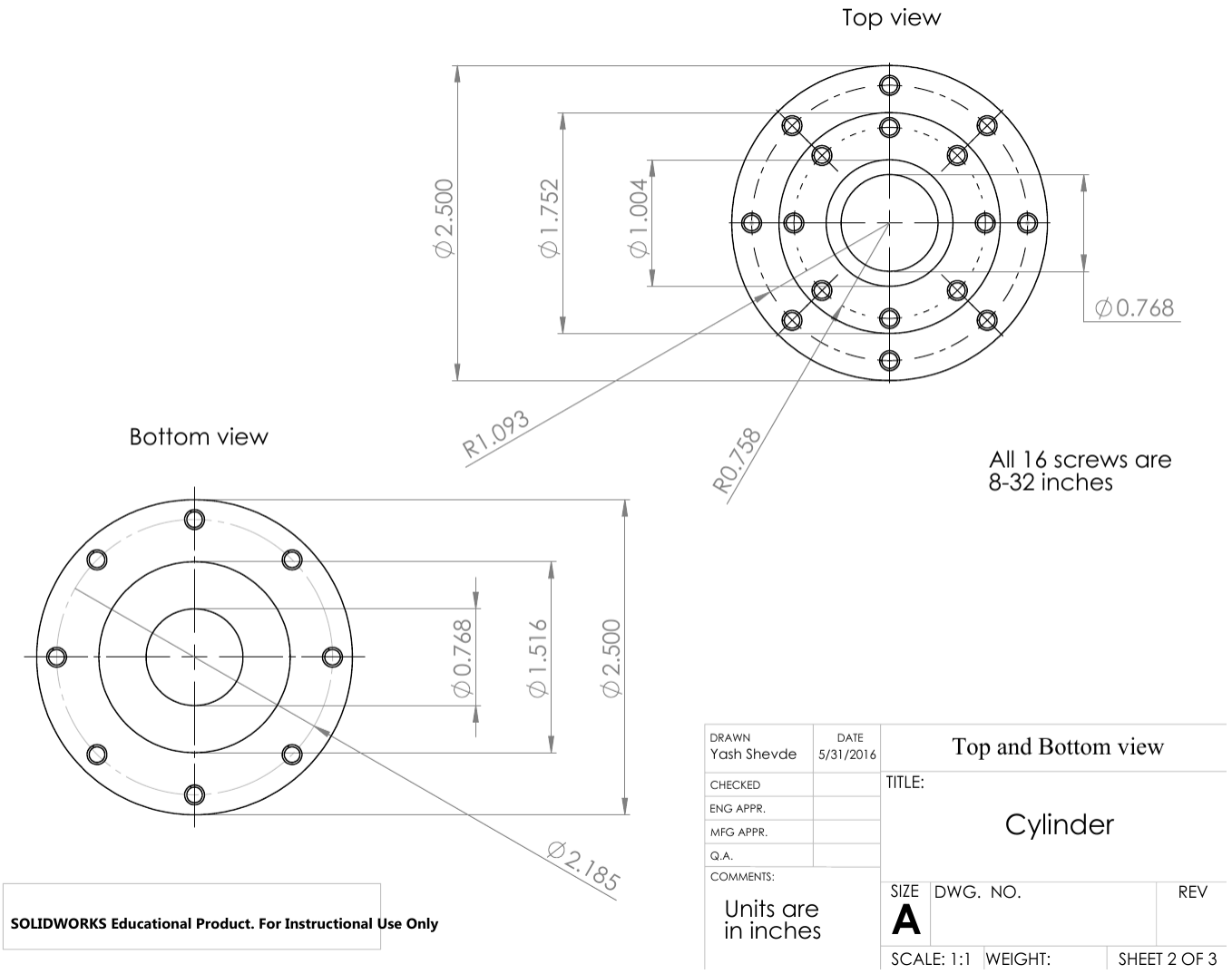

FIG. 15. The drawing of the cylinder end cap for solid ammonia making.

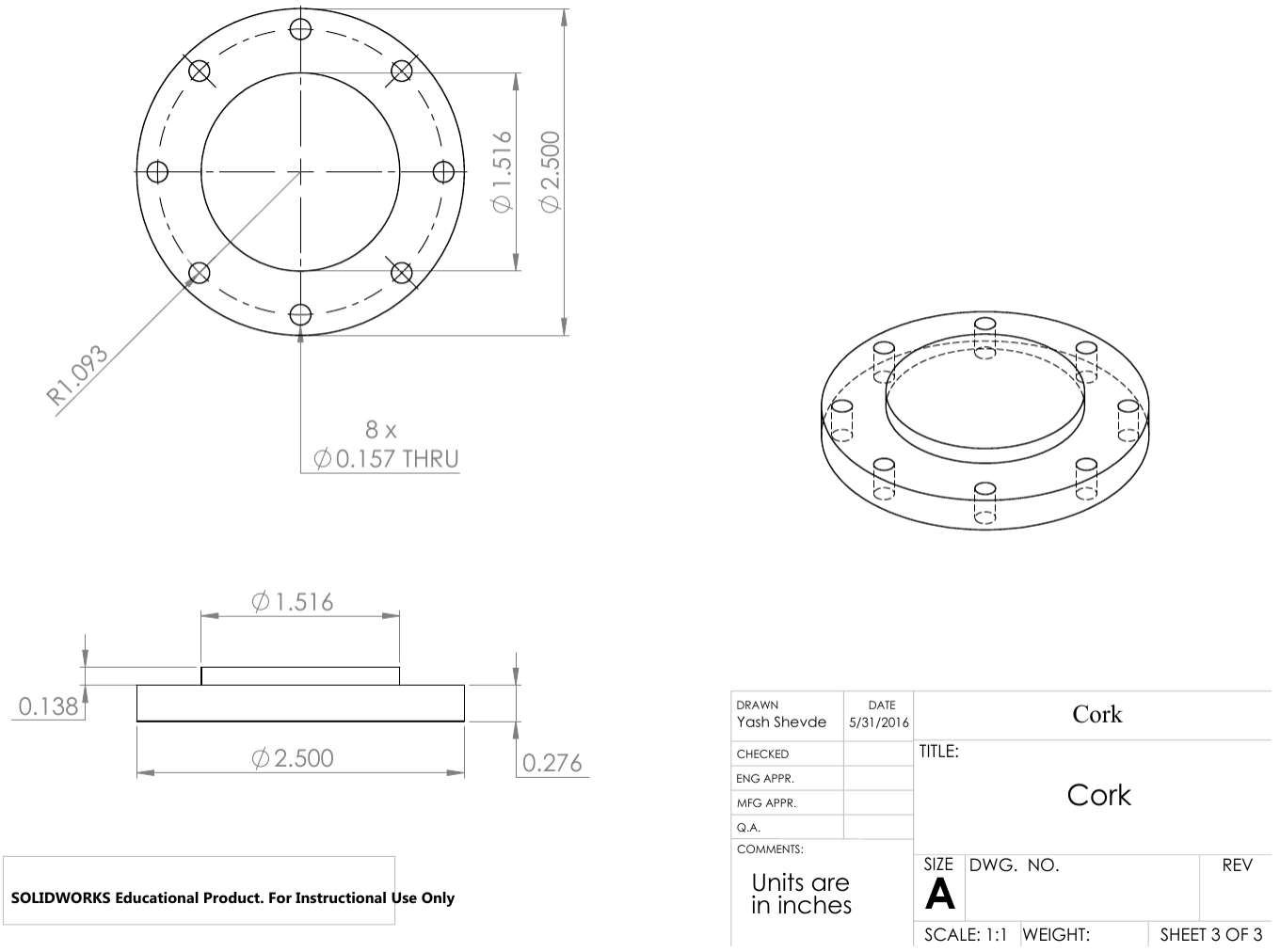

FIG. 16. The drawing of the cylinder end cap for solid ammonia making.