# Effect of Moisture in Ammonia on LED Device Performance and Impurity Control Through Liquid Extraction Total Vaporization Delivery and Purification Technologies

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## Introduction

Oxygenated impurities are particularly detrimental in GaN MOCVD. Incorporation of oxygen into nitride layers from impurities such as moisture in the process ammonia not only lowers the brightness of LEDs but also affect process yield. Therefore it is important to understand at what level the critical impurities affect devices and how the concentration of the impurities change during delivery of the ammonia, in order to implement effective impurity control technologies.

## I. Effects of Moisture in $NH_3$ on LED Structures

InGaN/GaN multi-quantum well LED structures were grown at 740ºC using TMG, TMI and 5N grade ammonia. Moisture was added to the ammonia at concentrations from 12.5 ppb to 2500 ppb to investigate its effect on the device electroluminescence (EL). The moisture doped ammonia was used in the growth of the InGaN/GaN MQW layer, the p-type AlGaN electron blocking layer, and the p-type GaN contact layer.

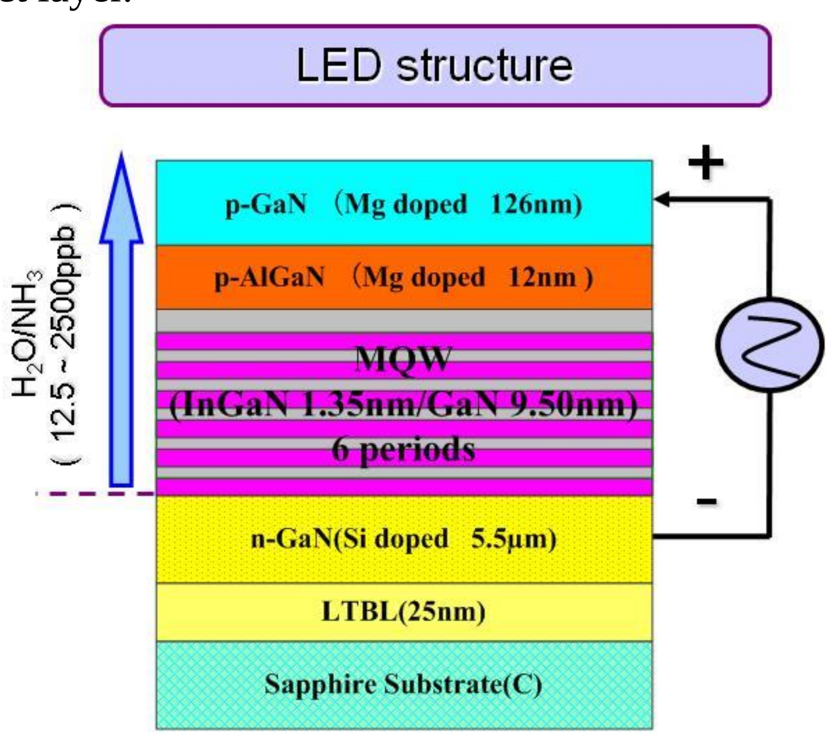


Figure 1: Schematic diagram of LED structure.

### A.SIMS Results

Oxygen levels in the AlGaN/GaN and MQW were elevated above baseline from moisture doped $NH_3$, even at 100 ppb.

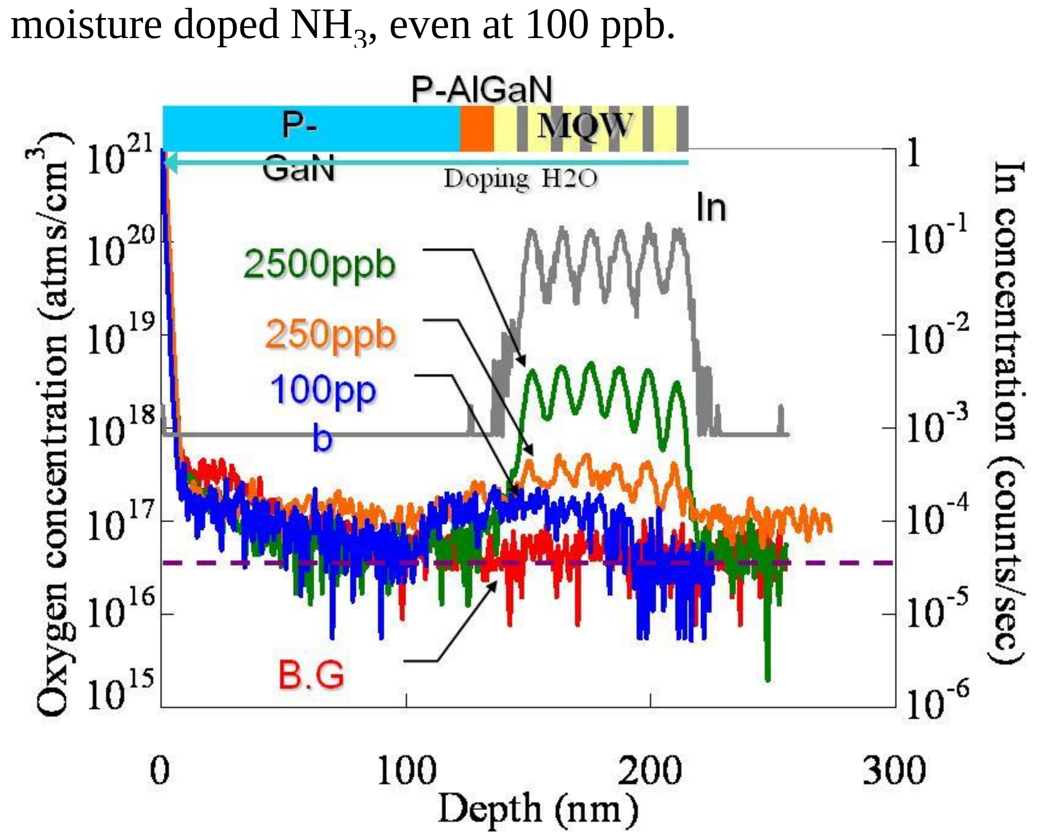


Figure 2: Oxygen concentration in LEDs fabricated using $NH_3$ with various $H_2O$ concentrations.

SIMS results reveal that the moisture doped ammonia is proportional to the oxygen levels found in the MQW layers of the LED, from ~1 x $10^{17}$ with 12.5 ppb $H_2O$ to ~5 x $10^{18}$ at 2500 ppb $H_2O$.

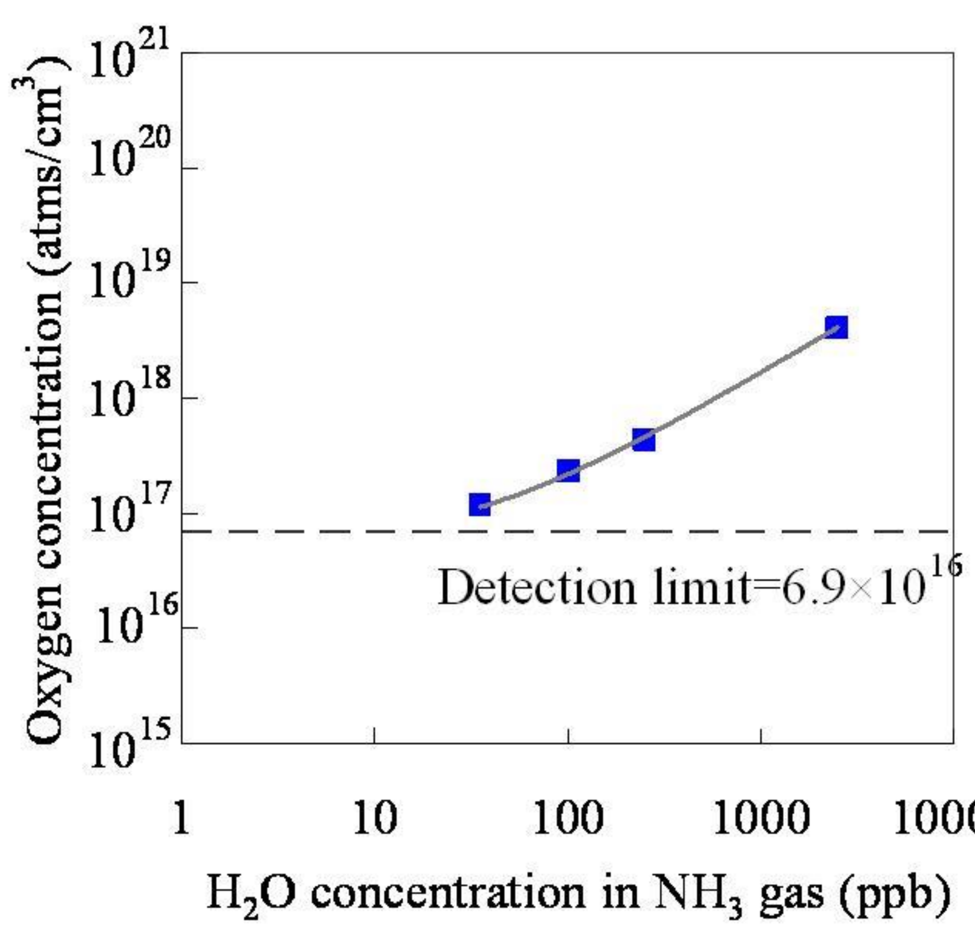


Figure 3: Oxygen concentration in the MQW layers as a function of $H_2O$ concentration in $NH_3$ gas.

### B. Electroluminescence

The moisture concentration was found to significantly affect the EL intensity. At 12.5 ppb $H_2O$, EL intensity was close to that of the background. However at 100 ppb $H_2O$, a ~30% decrease in relative intensity was observed and at 1000 ppb, the EL dropped to ~15% of the original intensity.

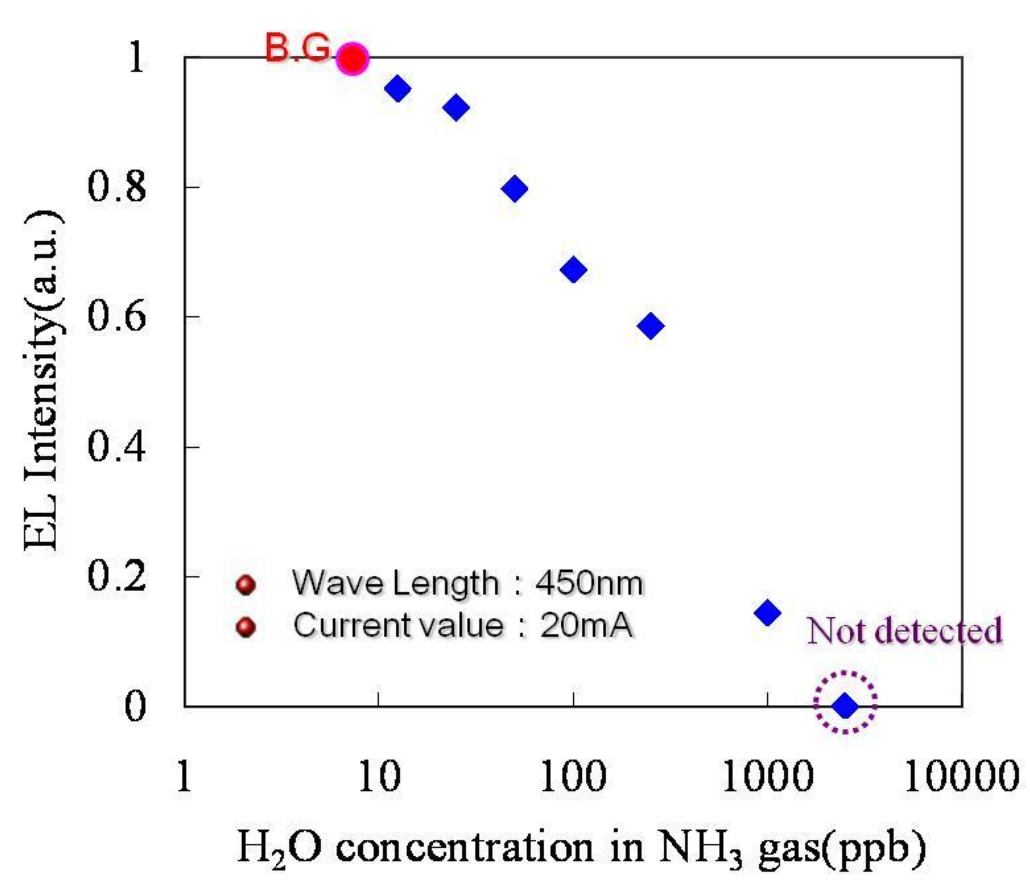


Figure 4: EL intensity as a function of $H_2O$ concentration in $NH_3$ gas.

### C. Purifier Performance to Remove Doped $H_2O$

Use of an NHX-Plus purifier or an TNSC SPMP purifier to remove the doped moisture from ammonia resulted in baseline EL intensities, thus were effective in removing the added moisture.

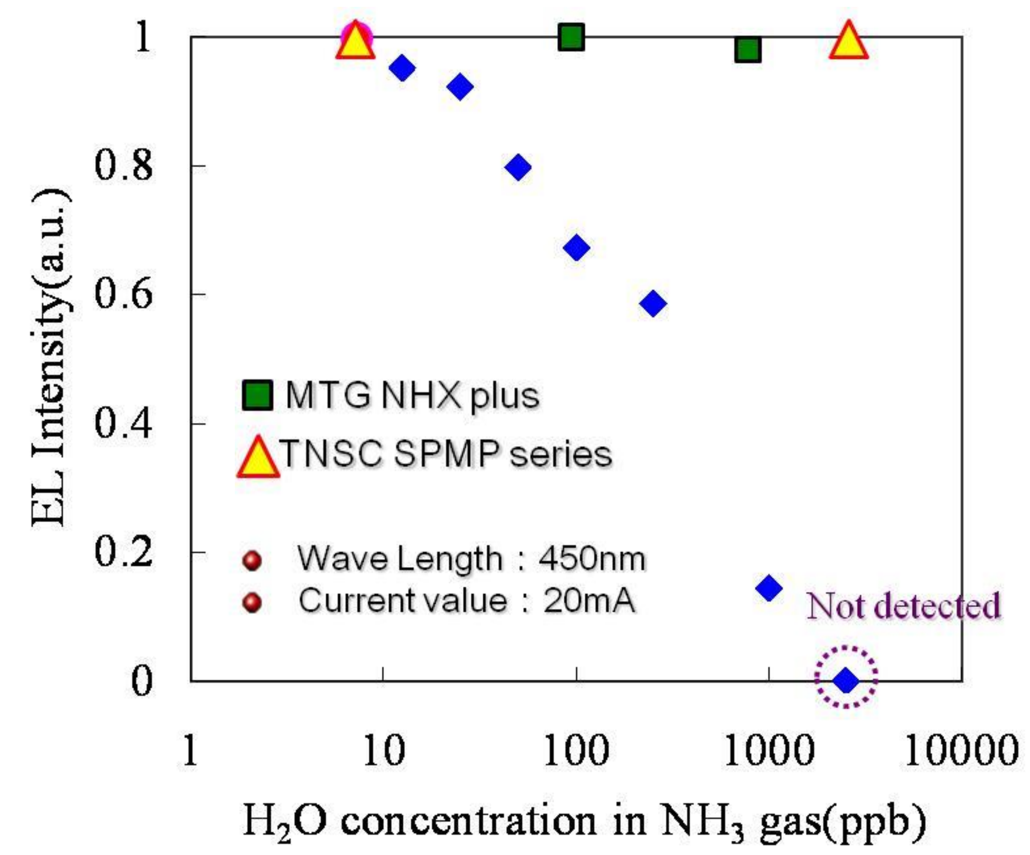


Figure 5: EL intensity vs. doped moisture concentration in $NH_3$ with purification moisture.

SIMS data also indicated that moisture was removed from ammonia to baseline levels by an NHX-Plus purifier at challenges up to 1 ppm.

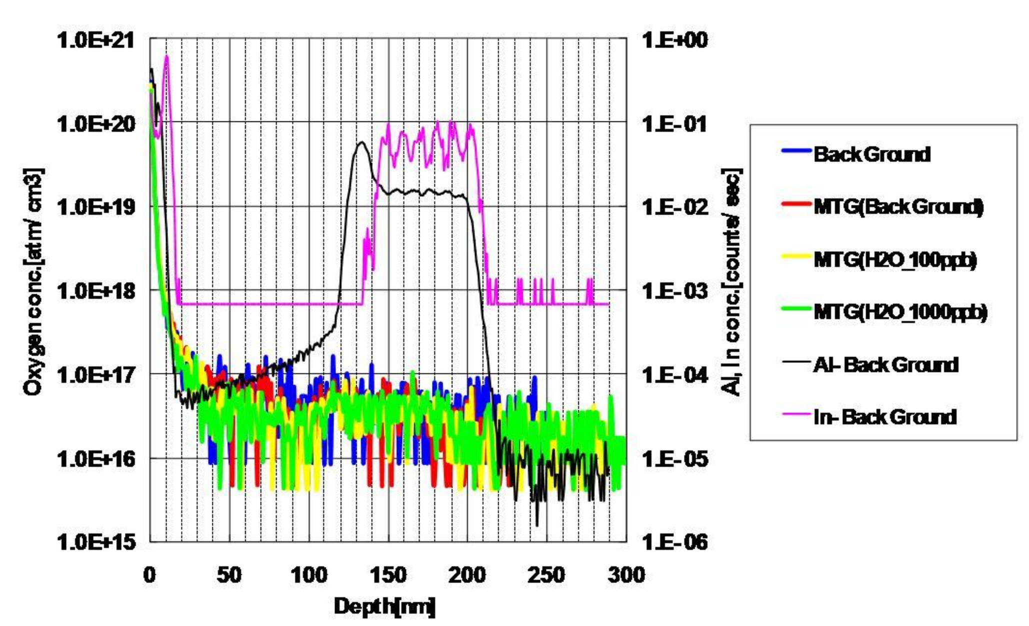


Figure 6: Oxygen levels with NHX-Plus moisture removal from ammonia at 100 ppb and 1000 ppb.

## II. Controlling Moisture in Ammonia through LETV Technology

The concentration of $H_2O$ delivered in ammonia can vary greatly depending on the delivery conditions. $H_2O$ partitions between the vapor and liquid phases and increasing $H_2O$ is observed as gas phase is withdrawn from the source, especially close to and after the phase-break point. Further, $H_2O$ levels are affected by the flow rate and temperature of the ammonia when delivered via gas phase. In contrast $H_2O$ must be controlled to low and sub-ppb levels in delivered ammonia for MOCVD. Introduction of purification technologies should be implemented for process consistency.

### A. Standard Gas Phase Delivery of Ammonia

Gas phase withdrawal concentrates moisture in the liquid phase causing unstable moisture in delivery.

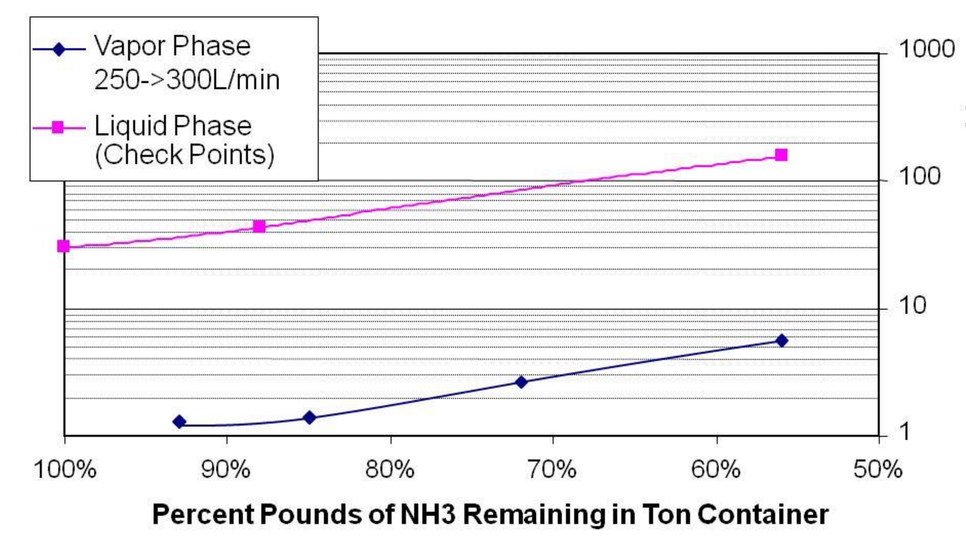


Figure 7: Moisture in ammonia vs. percent pounds of ammonia remaining in a standard tonner from *GAS* phase delivery.

Moisture concentration in ammonia is very dependant on flow rate when delivered via the gas phase.

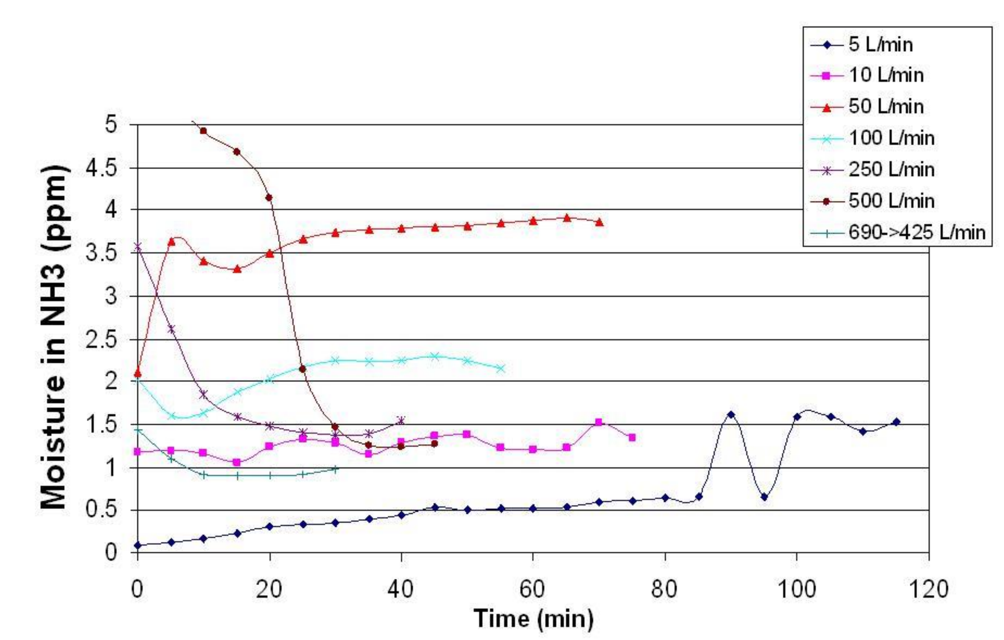


Figure 8: Moisture in ammonia vs. flow rate of ammonia from *GAS* phase delivery of a ton unit.

### B. Conventional Liquid Phase Delivery "Pot Boiler"

There are conventional types of liquid extracting ammonia from a vessel and vaporizing. These types of system use 'pot boiler' type vaporizers. This type of system also gives very unstable moisture levels.

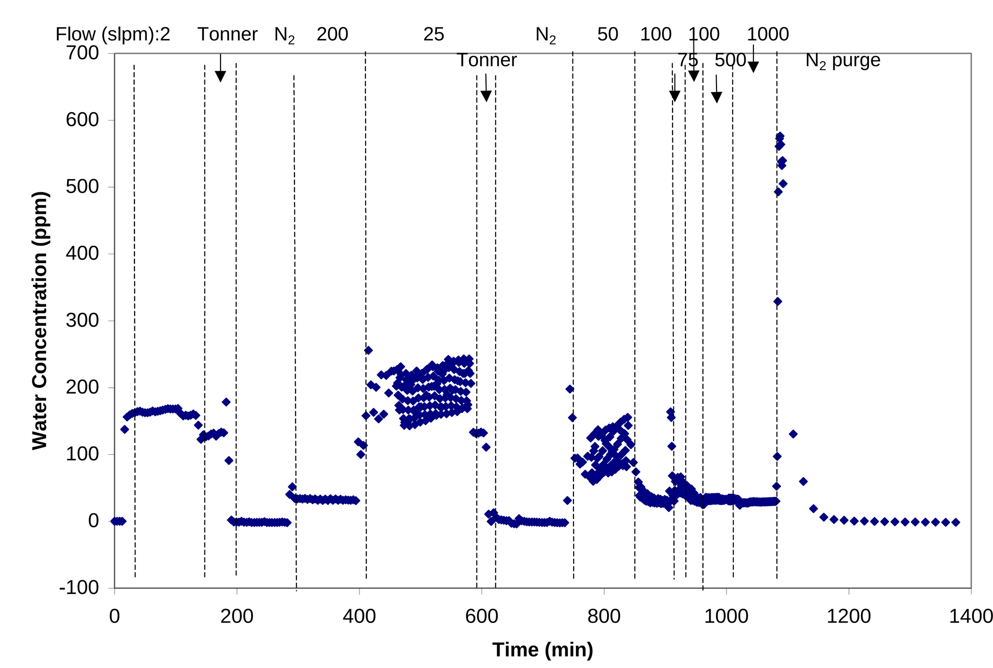


Figure 9: Moisture in ammonia as various flow rates from liquid extraction and using *CONVENTIONAL* vaporization

### C. LETV, Liquid Extraction Total Vaporization, of $NH_3$

LETV of the ammonia results in a stable $H_2O$ concentration as liquid is withdrawn from the vessel. Testing of an LETV delivery system shows consistent $H_2O$ levels as a unit was consumed 97%. This stable delivery allows POU purifiers to run consistent.

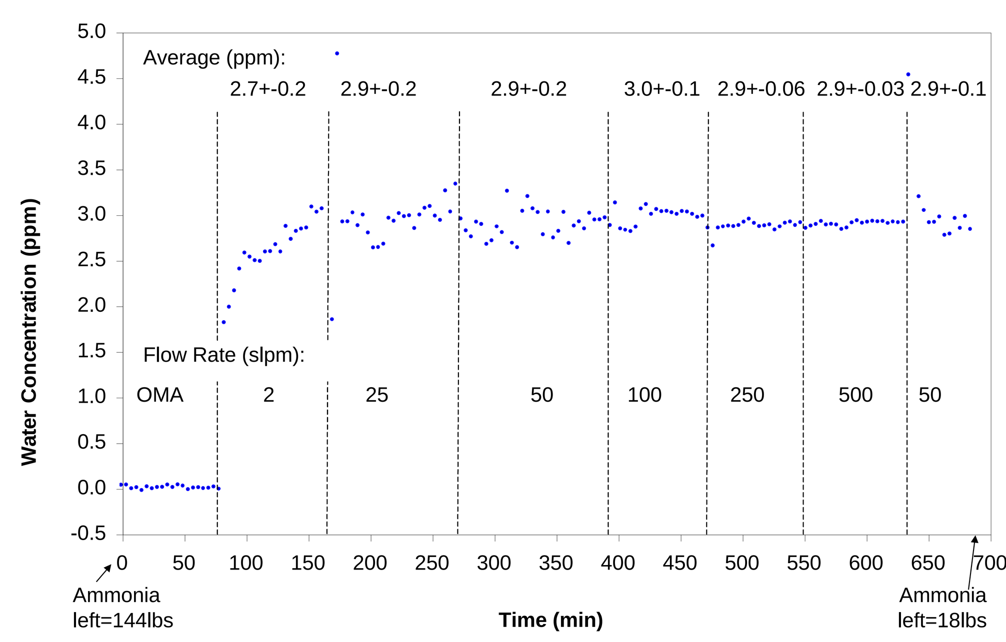


Figure 9: Moisture in ammonia at various flow rates from an LETV system.

LETV systems can be configured for various delivery applications; cylinder, ton unit, ISO, even plant size. LETV systems can be placed at the source or extended distances away to give the benefits of moving a liquid around a facility instead of a gas.

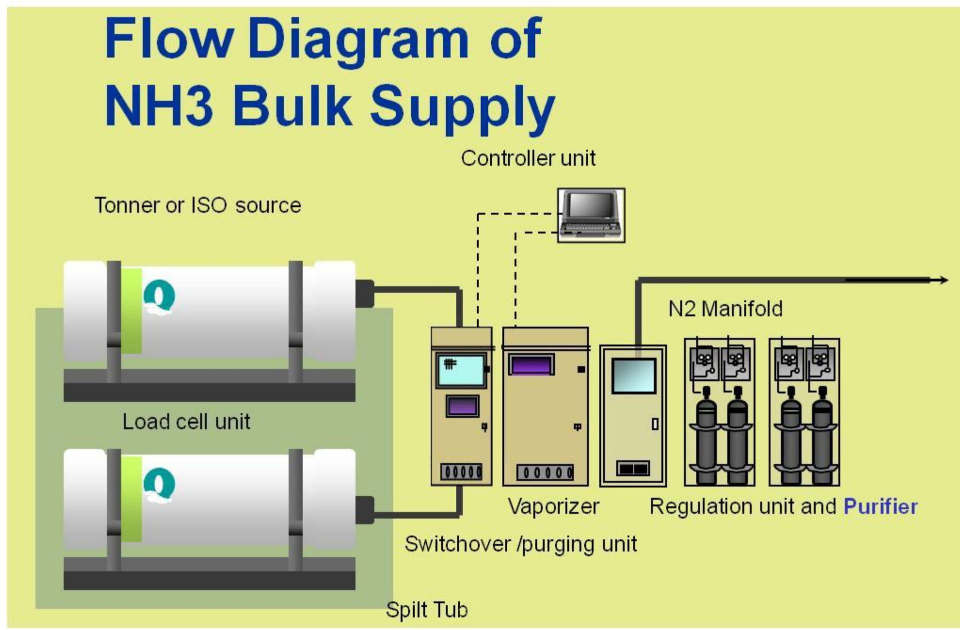


Figure 10: General flow diagram of an LETV bulk delivery system.

## IV. Conclusion

Growing LED's with added moisture in the ammonia displayed that oxygen was easily incorporated into MQW structure layer, which in turn directly effected the EL performance of the LED. Thus, minimizing the concentration of residual oxygen enables realization of high-efficiency LEDs. This minimization can be accomplished through the use of purification, as NHX-Plus and TNSC SPMP was shown to give baseline SIMS, EL values. And, utilizing an LETV system to delivery ammonia gives stable moisture levels throughout the usage of the container, allowing for predictable efficiencies and life times from purifiers.