



Selective measurement of ammonia isotopes by using photoacoustic spectroscopy

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Introduction – Different application areas, whether industrial or environmental requires a fast and automatic NH₃ detection system, which can reliably measure its concentration at sub ppm levels be it as a gas or isotopes without interference of common contaminants. One notable area is the electrochemical synthesis of NH₃, a field that is still largely in the research and development stage and shows great promise of substituting the Haber-Bosch process which has been reported to be energy intensive and a significant contributor to climate change due to its high greenhouse gas emissions. A major concern of the electrochemical synthesis process, is the low (< 1ppm) NH₃ generated whose detection and measurement is a challenge. Recent studies have highlighted the need to detect ¹⁵NH₃, in the presence of ¹⁴NH₃ and N₂ gas to guard against false-positive results, while providing information on the presence of contaminants [1].

Currently, several field and analytical methods have been employed for NH₃ isotopic measurements largely depending on their availability, cost and purpose (e.g., monitoring, process control etc.) [2]. Greatest disadvantage of these methods is the inability to suppress water signal in order to quantify the ¹⁵NH₃ signal owing to the small mass difference between H₂O and ¹⁵NH₃, which causes uncertainties in the detection of ¹⁵NH₃ at low ammonia concentrations. This work therefore seeks to design and construct a near infra-red diode laser-based photoacoustic (NIR-PA) system capable of selectively measuring and differentiating between ammonia gas isotopes (¹⁴NH₃ & ¹⁵NH₃) which will be useful in the detection and quantification of the discharged ammonia gas during the electro-reduction process of nitrogen gas and water or steam.

Methods – A multi-wavelength measurement was incorporated, first to suppress the spectral interference, secondly, to improve the sensitivity of the ammonia isotope measuring NIR-PA system and lastly to be able to measure different components simultaneously. This was achieved by using a longitudinal differential PA cell operating in the first longitudinal resonance (0,0,1 mode) with a cell constant of $C \approx 20 \text{ mV/cm}^{-1}/\text{Mw}$ as a detection unit. A laser beam was projected through a window on one side of the chamber, made of quartz glass and coated with an anti-reflection layer, parallel to the longitudinal axis and exited on the other side where a back reflecting mirror was mounted on the window. The purpose of the mirror was to increase the signal to noise ratio by doubling the path through which light was absorbed within the PA cell. Next, a widely tuneable external cavity diode laser (ECDL) was used to identify possible wavelength ranges which were optimal for NH₃ isotope sensitive detection, while avoiding interference with water vapor. A coupled Distributed Feedback laser operated in a wavelength modulated mode was then employed to tune the laser wavelength on the sub-second timescale by varying its driving current rather than using the much slower temperature tuning. This enabled the system to achieve maximum sensitivity. The experimental setup used for the ¹⁴NH₃ and ¹⁵NH₃ spectra measurements and calibration consisted of two main parts; the mass-flow controller mixing mode and the chemical reaction-based mode which offered the possibility of generating various

mixtures of the $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ to the NIR-PA system, operated either by an ECDL or by a DFB diode laser.

Results – The developed NIR-PA system was able to identify four wavelengths within the range of 1531.3 nm -1531.8 nm using both the ECDL and DFB diode laser as shown in Figure 1.

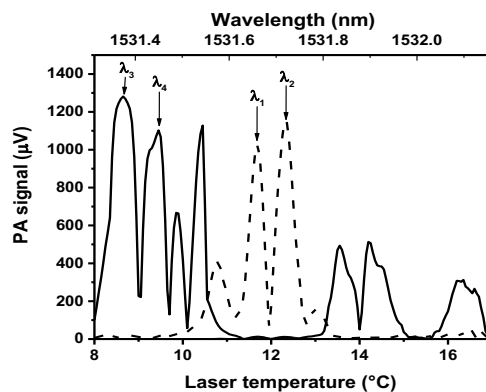


Fig. 1: PA spectra of the ammonia isotopes as recorded by DFB diode laser temperature tuning. Solid and dashed lines are the recorded spectrum of $^{15}\text{NH}_3$, and $^{14}\text{NH}_3$, respectively. The two wavelength pairs used for selective determination of the $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$ isotope concentrations are indicated as λ_1 , λ_2 and λ_3 , λ_4 respectively.

Upon current tuning this wavelength range and optimising the modulation parameters using the DFB laser, the system achieved a detection limit and sensitivity of 0.15 ppm and 6.3 $\mu\text{V}/\text{ppm}$ for $^{14}\text{NH}_3$ and 0.73 ppm and 1.3 $\mu\text{V}/\text{ppm}$ for $^{15}\text{NH}_3$ (with an inaccuracy below 0.1%), response. The response of the system to sudden concentration variation was 3.5 sec.

Conclusions – The NIR-PA system presented has proven to be capable of sensitively and selectively measuring $^{15}\text{NH}_3$ from a mixture of isotopically labelled NH_3 gas. The system is also robust, highly responsive and has very low cross-sensitivity to water vapour. This makes it ideal for the targeted application i.e. electrochemical synthesis of NH_3 .

References

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