Thesis Booklet

DEVELOPMENT OF A PHOTOACOUSTIC SYSTEM FOR THE SELECTIVE DETECTION AND ANALYSIS OF AMMONIA GAS ISOTOPES

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Szeged, 2022

1. Introduction

Globally, the need for green energy to combat or drastically reduce greenhouse gas emissions has in this century intensified in the hopes of tackling the climate change problem. One such gas is carbon dioxide (CO_2) which is a major by-product in the industrial ammonia (NH_3) production, Haber-Bosch process, with an annual output of 300 million Metric tons. Although ammonia is an important compound with applications ranging from the chemical, food and beverage, automotive and agricultural industries, its production process has been documented to be highly energy-intensive. The Haber-Bosch process also makes use of high temperatures (~ 450 ^oC) and pressures (~ 20 – 40 MPa) while consuming a big percentage of the earth's fossil fuel (natural gas (50%) or coal (19%)) as feedstock thus making it unsustainable and less environmentally friendly [1].

To tackle this concern, scientists and researchers have developed an alternative method for NH_3 production, namely through electrochemical synthesis. This method although still in the research and developmental stage, has shown great potential and is deemed less polluting and environmentally sustainable. This is because it has a provision for the direct conversion of renewable energy into chemical energy (in form of NH_3) with minimal or zero CO_2 emission. While the process has produced promising results, several problems have been identified of main concern being its low efficiency (0.1% – 8%) and inaccuracy in the assessment of NH_3 levels produced [2]. The latter problem is mostly due to the inability of the current NH_3 detecting equipment and analytical methods to reliably measure the low NH_3 gas produced (sub-ppm levels) without interference from common contaminants. NH_3 being the most abundant alkaline gas in the atmosphere means that it exists almost everywhere and distinguishing between the NH_3 generated by the electrochemical synthesis and general sources e.g. air, human breath, N_2 gas sources used in the synthesis process etc., requires very selective and sensitive analytical methods/equipment. So far, the employed analytical methods especially in spectroscopy are either all very expensive, need large sensing volumes (nuclear magnetic resonance), have uncertainties at very low NH_3 concentrations (molecular spectroscopy), or are limited by the availability of the tunable laser light at the appropriate wavelength (cavity ring-down spectroscopy), or simply have a problem in the control of its background signal (chemical ionization mass spectrometry).

In practice, accurate determination of the generated NH_3 from the electrochemical synthesis process has been a challenge which my studies seek to address and contribute a solution to.

2. Objectives

My main aim was to develop an instrument for the photo-electrochemistry application based on the photoacoustic spectroscopy concept, capable of continuous gas concentration measurement and selective differentiation between the ammonia gas isotopes.

Moreover, to achieve the above aim, there was a need for methodological development, construction of the measuring instruments and finally, the development of gas sampling procedures to be used. The following sub-aims were therefore carried out:

- Design and construction of a NIR-PA system capable of selectively measuring and differentiating between ammonia gas isotopes ($^{14}NH_3$ & $^{15}NH_3$).
- Selection and optimisation of the measurement and modulation parameters (wavelength, laser operating temperature, etc.).
- Construction, testing and calibration of the newly developed NIR-PA system.
- Solving the incidental problems and improvement of the system by re-optimisation of the selected parameters.

3. Applied Experimental Methods

Photoacoustic (PA) spectroscopy which is an optical absorption spectroscopy technique that indirectly measures optical absorption by converting the absorbed light energy into sound energy, has shown a great ability to detect NH_3 at very low sub-ppm concentrations. The standard PA measurement set-up contains a light source (e.g., laser), a PA cell, an electronic driver and a gas sampling unit. The sampled gas is introduced into the PA cell, the PA signal is generated there and measured by microphones attached to the cell. The generated sound signal by the PA effect is normally low, so amplifying and signal processing is required. The acoustic resonator, which amplifies the generated acoustic signal, and optical windows through which light enters and leaves the cell are set inside the photoacoustic cell. Other installations include acoustic filters (i.e., specially designed buffer volumes and low-pass filters), gas connections to the gas sampling system and a pump which can also be set depending on the target of the measurement to be done.

Several important quantities are usually analysed. One of them is the signal-per-noise ratio. The better the signal-per-noise ratio is, the higher the sensitivity of the concentration measurement. Another quantity is the minimum detectable concentration (MDC) of a photoacoustic system which is calculated as a ratio of the three times scatter of the background signal (background noise) divided by the sensitivity. The MDC simply denotes the detection limits of the PA system in the ppm or certain cases sub-ppm concentration range. Lastly and most important quantity to be analysed is the photoacoustic signal measured in mV and defined as the amplitude of the Fourier component of the microphone signal at the frequency of light modulation.

For the last two decades, the PAS Research Group at the University of Szeged of which I am now a member, have dedicated itself to researching, developing and providing applications for their various PA systems. In light of this, my thesis study has focused on the development of the near-infrared (NIR) PA detection method in the making of a detection system capable of selectively and sensitively differentiating between the NH_3 gas isotopes at relatively low concentrations. As part of the preliminary study, several important factors were considered during the design of the NIR-PA system. These included;

- The choice of the wavelength ranges to be used.

I did a literature review and found spectra data for both $^{14}NH_3$ and $^{15}NH_3$ isotopes. I then performed photoacoustic spectroscopy measurements on the isotopes at 1532 nm wavelength. These measurements were based on a telecommunication-type distributed feedback diode laser in a fibre-coupled construction.

- The choice of integrated electronics.

I assembled and settled on the integrated electronics manufactured by VIDEOTON HOLDING Ltd., Hungary, due to its inbuilt primary functions i.e., temperature control of the laser and PA cell, amplification and filtration of the microphone signal and the modulation of the diode laser driving current. Its operation was controlled by measurement software built from a set of subroutines using the Python programming language.

- The choice of light sources to be used.

I settled on the use of two laser light sources, i.e., a tunable external cavity diode laser (ECDL) and a distributed feedback (DFB) diode laser. I used the ECDL laser to identify the first optimal measurement wavelengths under amplitude modulation, and the DFB diode laser to further

optimise the identified wavelength range in conjunction with wavelength modulation. This was to find cross-interference-free wavelengths of both NH_3 isotopes to be used in the NIR-PA measurements.

- ❖ The choice and installation of the gas handling unit materials.

I chose (PTFE) material for the gas pipe tubing, with minimal length size, and low gas flow rates (150 ml/min) to minimise the effect of the system's response time. I also chose to use the PA cell (made of stainless steel) generally used by the PAS research group at the University of Szeged. This was heated to (50 $^{\circ}$C) with the main goal of minimising the adsorption-desorption processes brought about by the highly polar NH_3 molecules thereby reducing the measured gas temperature variations and holding it constant.

4. New Scientific Results

I. Selection of the wavelength and optimisation of the laser modulation parameters

1. Wavelength parameters.
   - I recorded the spectra measurements of $^{14}NH_3$ and $^{15}NH_3$ at wavelength 1470-1590 nm with an ECDL, and based on the data results, **I selected 1520-1523 nm and 1530.5 - 533.5 nm wavelength ranges** for further optimisation. Two DFB lasers were used to determine $^{14}NH_3$ and $^{15}NH_3$ absorption lines at the latter wavelength range. These lines did not overlap with absorption lines of water vapour by searching in a less than 1 nm wide wavelength range.

   - **I have also performed wavelength modulation on the designed NIR-PA system using DFB diode lasers.**

Since the optimum measurement wavelengths of both NH_3 isotopes lay sufficiently close to each other, the application of temperature tuning during wavelength modulation was made possible. Here, the **1530.5 - 1533.5 nm** wavelength range was chosen as the **optimum range** since suitable cross interference-free absorption lines were found unlike in the 1520 - 1523 nm wavelength range.

2. Laser operating temperature and current (I_{AC} & I_{DC}) values.

In determining the optimum parameters to be used by the lasers, I varied the values of laser modulation current i.e., both modulated (I_{AC}) and unmodulated (I_{DC}), together with the laser temperature producing a maximum PA signal.

- **For the DFB diode lasers, I varied the I_{AC} values between 2.3 – 22.9 mA such that at any given time, the total sum of $I_{AC} + I_{DC}$ was always 300 mA (maximum applicable current). After measuring the magnitude of the PA signal value at the maximum determined NH_3 absorption line, from each of the different sets of $I_{AC} + I_{DC}$ variations, I then identified the maximum peak signal of each laser. These optimum values were $I_{AC} \approx 9.1$ mA and $I_{DC} \approx 290.1$ mA.**

II. Calibration of the newly developed NIR-PA system.

I have prepared NH_3 gas mixtures using different percentages of ammonium chloride containing ^{14}N and ^{15}N marked isotopes intended to span a wide range of generated gas isotopes. From this;

- **I have calibrated both the $^{14}NH_3$ and $^{15}NH_3$ gas isotopes. A minimum detectable concentration of up to 0.28 ppm (3б) and 1.7 ppm (3б) for $^{14}NH_3$ and $^{15}NH_3$ respectively was measured.**

III. Design and construction of a NIR-PA system capable of selectively measuring and differentiating between ammonia gas isotopes ($^{14}NH_3$ & $^{15}NH_3$).

I have built a highly selective NIR-PA system, a feature that enables it to not only distinguish between the $^{14}NH_3$ and $^{15}NH_3$ isotopes but also detect and keep interference from other molecular species (cross-sensitivity effects) at a minimum level; especially water vapour. The system is also stable which ensures that lengthy and continuous measurements (2-3 months) can be done after the initial calibration which depicts linearity over 3 orders of magnitude.

IV. Improvement of the newly developed NIR-PA system.

I have improved the response time of the system by the addition of a diffuser into the PA cell and the application of current tuning instead of the previously used temperature tuning during wavelength modulation.

This made it possible to program the operational software of the NIR-PA system in a way as to complete a single concentration measurement cycle on the four selected wavelengths in less than a second. This improved the **response time of the system which was calculated as 3.5 seconds as compared to 24.4 seconds found by the preliminary NIR-PA system.**

I have improved the sensitivity of the system by an order of magnitude by fibre coupling two lasers together, applying a back-reflecting mirror to the PA cell and subtracting PA signals with opposite phases.

- I have improved the MDC from 0.28 ppm and 1.7 ppm (3б) for $^{14}NH_3$ and $^{15}NH_3$ respectively in the preliminary NIR-PA system without a back-reflecting mirror, to **0.14 ppm and 0.73 ppm (3б) for $^{14}NH_3$ and $^{15}NH_3$** in the new NIR-PA system with a back-reflecting mirror installation.

- I have improved the MQC values from 0.92 ppm and 5.5 ppm (3б) for $^{14}NH_3$ and $^{15}NH_3$ respectively in the preliminary NIR-PA system without a back-reflecting mirror, to **0.48 ppm and 2.43 ppm (3б) for $^{14}NH_3$ and $^{15}NH_3$** respectively after modifications and improvement to the NIR-PA system.

- I have calculated the cross-sensitivities of the isotopes as **-1.3×10^{-4} ppm/ppm for the value of $^{14}NH_3$** due to the presence of $^{15}NH_3$, and **7.4×10^{-3} ppm/ppm, for the value of $^{15}NH_3$** due to the presence of $^{14}NH_3$, respectively.

5. Applicability of the new scientific results

Due to my developed NIR-PA systems' robustness, high sensitivity, low cross-sensitivity, and short response time it is expected to find a practical application in the detection and measurement of isotopically labelled NH_3 gas which has been discharged from an electrochemical synthesis process. This will enable it to distinguish with certainty between the ammonia gas produced and the general probable contaminants.

Another planned application is in the agricultural sector where the system can be used to investigate both soil and plant physiological processes. This would involve the isotopic tracing of the denitrification process in the soil/vegetation by application of ^{15}N labelled fertilizer to estimate the nitrogen loss in form of ammonia. The transformation of soil N, like denitrification or the N fixation by plants, could also be traced by this technique.

The developed system is also expected to find an application in the source apportionment of atmospheric ammonia concentrations. The change in abundance ($\delta^{15}NH_3$, ‰) i.e., the source signature is representative of the given physical and chemical process. Identifying the ammonia source (e.g., agricultural or fossil fuel combustion process, industry, heating, traffic) by nitrogen isotope helps in designing a mitigation strategy for policymakers.

6. References

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6. Publications and Conference Participation

Hungarian Scientific Bibliography (MTMT) Author ID: 10082771

Publications and conferences related to the scientific topic of the dissertation:

[1]. ***Emily Awuor,*** *Helga Huszár, Zoltán Bozóki*

Measurement of Ammonia Isotopes ($^{14}NH_3$ and $^{15}NH_3$) using Photoacoustic method, // **évkönyv**. (2021), p. 208 – 220. (ISSN 2217-8198).

https://doi.org/10.18485/uns_evkonyv.2021.13

[2]. ***Emily Awuor****, Helga Huszár, László Horváth, Gábor Szabó, Csaba Janáky and Zoltán Bozóki*,

Development of a Near-Infrared Photoacoustic System for Selective, Fast and Fully Automatized Detection of Isotopically Labelled Ammonia, **Analytical Chemistry** (2022), https://doi.org/10.1021/acs.analchem.2c01191. ***(Q1, IF = 8.008)***

[3]. ***Emily Awuor,*** *Helga Huszár, László Horváth, Gábor Szabó, and Zoltán Bozóki*

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Accepted for publication. ***(Q4, IF = 0.896)***

Lecture:

Emily Awuor*, Helga Huszár, Tibor Ajtai, Gábor Szabó, Csaba Janáky and Zoltán Bozóki* "Selective Measurement of Ammonia Isotopes by Using Photoacoustic Spectroscopy", **ICPPP21,** International Conference on Photoacoustic and Photothermal Phenomena, (2022), Bled, Slovenia.

Posters:

Emily Awuor*, Helga Huszár*, *Csaba Janáky, Tibor Ajtai,* Gábor Szabó, *Zoltan Bozóki*
"Selective and Highly Sensitive Measurement of $^{15}NH_3$ Using Photoacoustic Spectroscopy for Environmental Applications", **ICAQMM 2021**; 23rd International Conference on Air Quality Management and Monitoring, May 03 – 04, (2021), Rome Italy. (Best Poster Presentation).

***Emily Awuor**, Helga Huszár, Zoltan Bozóki*

"Measurement of Ammonia Isotopes ($^{14}NH_3$ and $^{15}NH_3$) using Photoacoustic method", Organization for Women in Science for the Developing World (**OWSD) 6th General Assembly and International Conference**, November 8 – 19, (2021).

Other Lectures not directly related to Thesis Work.

***Emily Awuor**, Anna Szabo, Zoltan Bozóki*

Measurement of Aerosol from Exhaust Emission of Motor Vehicles using Photoacoustic Spectroscopy, **25th International Symposium on Analytical and Environmental Problems,** (2019), pp. 366 – 368, Szeged, Hungary.

ISBN 978-963-306-702-4.