Implementing a method based on near infrared spectroscopy for the “in-situ” determination of ammonia/water composition in an absorber test bench

M. Isabel Barba\textsuperscript{a}, Miguel Berdasco\textsuperscript{a}, Daniel Salavera\textsuperscript{a}, M. Soledad Larrechi\textsuperscript{b*}, Alberto Coronas\textsuperscript{a*}

Universitat Rovira i Virgili, Tarragona, Spain.
\textsuperscript{a}CREVER. Mechanical Engineering Dept. \textsuperscript{b}Analytical and Organic Chemistry Dept.

*Tel: +34 977 559 559, e-mail: alberto.coronas@urv.cat

Abstract. This study presents the first results of composition measurement in an ammonia/water mixture determined at real time using near-infrared (NIR) spectroscopy in an absorber test bench. Two cells were designed and constructed; a static cell for calibrating under controlled conditions of pressure, temperature and composition on a laboratory scale; and a dynamic flow cell for measuring in the absorber test bench. The ammonia absorption band was not significantly affected by the solution flow rate and neither by small variations in the temperature and pressure. A linear regression model between the absorbance value at 1033 nm and the ammonia concentration was established. This model was used to estimate the concentration in an ammonia/water absorber test bench. The methodology was validated by density measurements of the samples. The value of the mean deviation was 0.0024.

1. Introduction

Measuring the composition of the working fluid mixture in absorption refrigeration cycles is of great interest because it is a key parameter in performance [1]. In absorption refrigeration systems based on ammonia/water mixtures, analytical methods that can measure real-time concentration are needed and the most common approach uses density measurements.

Near-infrared (NIR) spectroscopy is a very well-known technique for in-situ analysis of the samples. It is non-destructive, measurements are nearly instantaneous and real time data is obtained [2]. The intensity of the absorption band around 1033 nm, attributable to the stretching vibration of the -NH functional group, can be used for quantitative analysis of the ammonia concentration in ammonia/water mixtures [3]. However, this technique has not yet been fully implemented in this area as an alternative to conventional analytical methods probably because no commercial measurement cells are available.

This study focuses on determining ammonia/water composition in an absorber test bench using the NIR spectroscopic technique. To do so, two stainless steel cells with two sapphire windows were designed and constructed: a static cell, for calibrating under controlled conditions of pressure, temperature and composition on a laboratory scale; and a dynamic flow cell for measuring the ammonia concentration in situ in the absorber test bench.

A preliminary analysis was made to evaluate the effect of the pressure, the temperature and the flow rate on the spectra. Then, a linear regression model between the absorbance at 1033 nm and the ammonia concentration in the mixture was established using the static cell. The model was used to determine the ammonia concentration of the solution in the absorber test bench using a dynamic flow cell. The methodology was validated by density measurements.
2. Experimental set-up

2.1. Experimental set up in the laboratory: Static cell with integrated NIR

Figure 1 shows a scheme of the instrumental set up used for establishing the calibration model on a laboratory scale.

![Figure 1](image)

This setup consists of a static cell (A) with two sapphire windows where the optical fibers are connected, a pressure transmitter (B) connected to a compressed nitrogen bottle (C), an auxiliary cylinder to introduce the ammonia (D), and a vacuum pump (E). The optical fibers are connected to a Maya 2000 Pro Vis-NIR spectrophotometer (F) with an HL-2000-CAL tungsten halogen light source (G) and a high-pass filter (>590 nm) (H). The spectrophotometer is connected to a computer for data acquisition.

To carry out the experiments, a 15-mL stainless-steel measuring cell was designed and built to withstand pressures of up to 2 MPa. This cell has two openings at the top. One is used to introduce the components (water and ammonia), and the other is used to pressurize and empty the cell. The experimental procedure used to prepare the ammonia/water mixture is as follows. First, the water content is introduced into the cell using a syringe. The mass of water is determined using an analytical balance (Mettler Toledo, mod. PR2003DR, resolution 0.1 mg). The desired quantity of ammonia is then introduced directly into an auxiliary cylinder using liquid nitrogen to make the sampling easier. The mass of ammonia in the cylinder is determined using a balance (Mettler Toledo, mod. ME2002, resolution 0.01 g). Next, the auxiliary cylinder is connected to the measuring cell immersed in ice and the valve is opened. The cylinder is heated to ensure that the maximum quantity of ammonia passes into the cell. Finally, the mass of ammonia remaining in the cylinder is measured to determine, by difference of mass, the quantity of ammonia introduced into the cell.

When the sample is ready, the static cell is immersed in a thermostatic bath (Lauda, mod. E106T) (J) to control the temperature of the experiment and then connected to the nitrogen line through a spiral-shaped tube. The purpose of this is to pressurize the cell and keep the samples liquid. The samples are stirred constantly (K).

2.2. Pilot plant experimental set up: Dynamic flow cell with integrated NIR

A new in-line dynamic flow cell was designed, built and installed in a pilot plant absorber test bench in order to determine the ammonia concentration in the system. Figure 2 shows a scheme of the
instrumental configuration in which the ammonia/water solution flows through the cell whereas the light coming from the source passes across the cell in order to be collected in the spectrophotometer.

Figure 2. Dynamic flow cell with integrated NIR: (A) Measuring cell. (B) Light source. (C) Filter. (D) Spectrophotometer. (E) Tube.

Figure 3 shows a scheme of the pilot plant absorber test bench in which the dynamic flow cell with integrated NIR (Figure 2) has been incorporated into the system for determining the ammonia composition. In this test bench a polymer membrane is used as a contactor between the ammonia vapour and the ammonia water solution in order to reduce the size of the absorber. Membrane absorbers have a higher surface/volume ratio than other conventional absorbers. The ammonia/water solution is pumped from the feed tank to the membrane absorber and heated up in the heat exchanger. Once in the absorber, the ammonia vapour stream from the bottle passes through the pores of the membrane and is absorbed into the solution, thus increasing its concentration and temperature. This rich solution is collected in the product tank. Figure 4 shows the dynamic flow cell already installed in the test bench.
2.3. Spectra and samples
Spectra were recorded between 990-1069 nm at intervals of 1 nm. All the original spectra were corrected using a weighted-least-squares baseline function [4] to eliminate any vertical shift in the spectra during the course of the experimental caused by the NIR spectrophotometer with only one light beam.

An ammonia/water mixture was analyzed in the pilot plant at different flow rates, pressures and temperatures in order to evaluate how these conditions affected the ammonia absorption band. The calibration was done in the laboratory, where five mixtures with different ammonia mass fractions (0.000, 0.373, 0.413, 0.433 and 0.508) were prepared and measured as described above (section 2.1).

3. Preliminary results
Figure 5 and Figure 6 show the spectra obtained during the analysis of a mixture in the dynamic cell at different flow rates (Figure 5), temperatures and pressures (Figure 6). Figure 5 shows that there are small

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Figure 3. Scheme of the absorber test bench with the dynamic flow cell with NIR integrated NIR

Figure 4. Stainless steel dynamic flow cell

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Figure 5 and Figure 6 show the spectra obtained during the analysis of a mixture in the dynamic cell at different flow rates (Figure 5), temperatures and pressures (Figure 6). Figure 5 shows that there are small
variations in the spectra at the maximum of the peak. However, these variations do not differ significantly from the variations obtained in the spectral region between 1000-1015 nm, where the variations are representative of the instrumental noise. The same behaviour can be observed in Figure 6. Thus, it can be concluded that the flow rate, temperature and pressure have a negligible effect on the spectra under the working conditions of interest.

![Graph showing absorbance vs. wavenumber for different mass flow rates](image1)

**Figure 5.** Spectra of the ammonia/water mixture at 1033 nm obtained at different mass flow rates

![Graph showing absorbance vs. wavenumber for different pressures and temperatures](image2)

**Figure 6.** Spectra of the ammonia/water mixture at 1033 nm obtained at different pressures and temperatures

Because the flow rate had a negligible effect, the calibration model was established under static conditions in the laboratory using the experimental configuration explained in section 2.1. Furthermore,
taking into account that the effect of the temperature and the pressure on the absorbance is also negligible, the absorbance only depends on the concentration of the sample. Figure 7 shows the linear regression between the maximum absorbance value of the peak at 1033 nm and the ammonia concentration of the samples. The values of the regression coefficients are also included in the figure.

![Linear regression between absorbance and ammonia concentration](image)

**Figure 7.** Linear regression between absorbance and ammonia concentration

Table 1 shows the absorbance values of the samples analyzed in the pilot plant with the dynamic cell and the ammonia mass fractions estimated using the calibration model or calculated from the density measurements [5].

| Sample | p(bar) | T(°C) | Absorbance | \(x_{\text{NH}_3}\) from NIR measurements | \(x_{\text{NH}_3}\) from density measurements |
|--------|--------|-------|------------|-----------------------------------------|-------------------------------------------|
| 1      | 3      | 24.9  | 0.3873     | 0.4280                                  | 0.4260                                    |
| 2      | 3      | 24.5  | 0.3931     | 0.4340                                  | 0.4340                                    |
| 3      | 3      | 25.0  | 0.3736     | 0.4130                                  | 0.4160                                    |
| 4      | 3      | 25.0  | 0.3744     | 0.4140                                  | 0.4100                                    |
| 5      | 3      | 25.1  | 0.3542     | 0.3920                                  | 0.3890                                    |

The regression line obtained when both ammonia mass fractions (\(w_{\text{NH}_3}\)) are compared is shown in Figure 8. The mean deviation in the data is 0.0024. In the usual working conditions this mean deviation value is acceptable.
Figure 8. Deviation between the concentration values obtained from density measurements and the concentration values obtained from the NIR calibration model.

4. Conclusions and future work
The preliminary results show that the mean deviation between the concentration values obtained from the reference measurements (density) and the concentration values obtained using the proposed methodology (NIR) is 0.0024. This deviation value is acceptable for the habitual working conditions in this application, so Near-infrared (NIR) spectroscopy is an appropriate technique for measuring the concentration of ammonia/water mixtures in real time. However it is important to highlight that this technique is still being studied.

5. Acknowledgements
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6. References
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