

# Development of an Analytical Method for Distinguishing Ammonium Bicarbonate from the Products of an Aqueous Ammonia CO<sub>2</sub> Scrubber

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The link between anthropogenic emissions of carbon dioxide, increasing atmospheric CO<sub>2</sub> levels, and concomitantly increasing global temperatures is established and accepted. The use of aqueous ammonia, to capture CO<sub>2</sub> and produce an inexpensive nitrogen fertilizer, ammonium bicarbonate (ABC), is believed to be a feasible approach to CO<sub>2</sub> sequestration. Due to the varying concentrations of reactants and varying reaction conditions, different ammonia–carbon compounds may be produced. ABC is the ideal product for maximizing NH<sub>3</sub> utilization in CO<sub>2</sub> capture; therefore, identification and quantification of ABC in the reaction products is mandatory. Various analytical techniques were used to distinguish and quantify the ABC. Fourier transform infrared spectroscopy can only be used to distinguish ammonium carbamate, and, X-ray diffraction can be used to qualitatively distinguish ABC from the other possible products of the CO<sub>2</sub> capture reaction. Carbon–hydrogen–nitrogen elemental analysis and near-infrared (NIR) spectroscopy were used to quantify ABC, with both techniques giving  $\pm 5\%$  agreement for ABC concentrations for 8 of 13 samples from a bench-scale aqueous ammonia CO<sub>2</sub> scrubbing system. An additional 3 of the 13 samples were within  $\pm 12\%$ . Results indicate that NIR will be an ideal tool for real-time, on-line measurements of ABC in a full-scale aqueous ammonia CO<sub>2</sub> scrubber. The ABC in 11 samples from the bench-scale scrubber at Western Kentucky University was determined by these techniques and assessed to have very good quality as a fertilizer in accordance with GB-3559-92, the Agricultural Ammonium Bicarbonate National Standard of China.

It has been known for more than 100 years that carbon dioxide is a greenhouse gas and that the release of CO<sub>2</sub> from fossil fuels may affect the climate of the earth.<sup>1</sup> The growing awareness of the risks of climate change has generated public concern, and since 1989, researchers have become more interested in seques-

tering CO<sub>2</sub>. As the world population increases and energy demand rises, increased burning of fossil fuels will continue to drive atmospheric CO<sub>2</sub> levels upward. Herzog and co-workers noted that power production contributes one-third of the CO<sub>2</sub> released from fossil fuel combustion worldwide.<sup>2</sup> Generation of CO<sub>2</sub> through fossil fuel combustion will remain a substantial contributor to the total amount of atmospheric green house gases. Capturing and securely storing carbon emitted from the global energy system is an important and attainable goal. Several researchers have proposed and developed possible solutions such as chemical solvents, physical absorption, cryogenic methods, membrane systems, and biological fixation.<sup>3–5</sup> Of these, the chemical solvent methods are currently recognized as the most effective technologies. The cost of capturing CO<sub>2</sub> can be reduced by finding a low-cost solvent that can minimize energy requirements, equipment size, and corrosion. An approach that may provide an inexpensive and effective route to reduce CO<sub>2</sub> emissions from power plants is extracting CO<sub>2</sub> with aqueous ammonia in a wet scrubber.<sup>6</sup> This technique presents many advantages for CO<sub>2</sub> capture over the monoethanolamine process due to its lower cost, higher CO<sub>2</sub> absorption efficiency and capacity, lower decomposition temperatures of ammonium bicarbonate (ABC), and less corrosive environment for the absorber material. Bai and Yeh<sup>7</sup> used breakthrough curves to determine that the NH<sub>3</sub> scrubbing capacity was 0.35 mol of CO<sub>2</sub>/mol of NH<sub>3</sub>, or 0.9–1.2 kg of CO<sub>2</sub>/kg of NH<sub>3</sub>, with a removal efficiency of  $\sim 99\%$ . Smouse and co-workers<sup>8</sup> proposed and developed a multipollution control concept using aqueous ammonia sprayed into actual flue gas to capture CO<sub>2</sub>, SO<sub>2</sub>, and NO<sub>x</sub> emissions with a CO<sub>2</sub> capture efficiency in the range from 76.4 to 91.7% at 35 °C.

Carbon dioxide can be removed from flue gases by ammonia scrubbing at various temperatures and operating conditions. Equation 1 illustrates ammonium carbamate (ACM; NH<sub>2</sub>COONH<sub>4</sub>)

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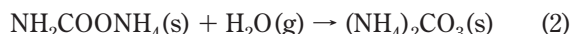
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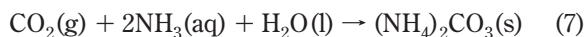
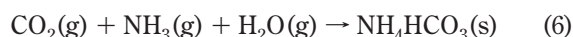
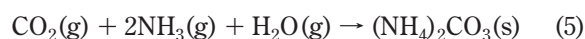
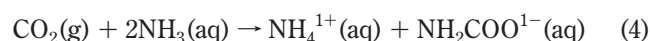
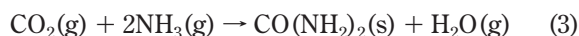
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is the main product in dry conditions under ambient pressure. However, ACM is very soluble in water and the hydration product ammonium carbonate (ACN;  $(\text{NH}_4)_2\text{CO}_3$ ) is produced at room temperature, as eq 2 shows.<sup>7</sup>



There are two major concerns with the dry condition. First, there is an explosion hazard with the dry  $\text{CO}_2$ – $\text{NH}_3$  reaction if the process is designed or operated improperly, as the explosive limit for  $\text{NH}_3$  gas is 15–28% (v/v). Second, passageway plugs in the reactor could cause the production to stop. For safety and simplicity, the wet method should be used.

The possible reactions between  $\text{CO}_2$  and  $\text{NH}_3$  and in a wet scrubber are illustrated by the following equations:<sup>7</sup>



At room temperature and atmospheric pressure, reactions 4–8 occur. In the wet scrubber, where  $\text{CO}_2$  is removed by  $\text{NH}_3$ , reactions 7 and 8 are dominant. These reactions are very complex, with many species and reactions coexisting in the solution. The effluent from an aqueous ammonia  $\text{CO}_2$  scrubber could include ABC, ACN, and ACM, all in crystalline or aqueous forms, plus residual reactants. Of the reaction products, ABC has been utilized by certain developing countries as a crop fertilizer for over 30 years with proven results.<sup>9</sup> ABC is the ideal product for maximizing  $\text{NH}_3$  utilization in  $\text{CO}_2$  capture, requiring a minimum  $\text{NH}_3$  inventory; therefore, identification and quantification of ABC in the reaction products is mandatory.

China has used ABC as the mainstay of nitrogen fertilizers for many years. Several analytical methods are used for determining ABC with the majority focusing on the ammonia or nitrogen content because ABC is used as a nitrogen fertilizer. The distillation and titration method distills the ABC from alkaline solution and absorbs the ammonia in excess standard sulfuric acid, which is then titrated with sodium hydroxide.<sup>10</sup> The nitrogen is calculated by the consumption of standard sulfuric acid. Diao and co-workers<sup>11</sup> proved that ABC is the main product of the  $\text{CO}_2$ – $\text{NH}_3$ – $\text{H}_2\text{O}$  reaction, using Fourier transform infrared spectroscopy (FT-IR) analysis. Bai and Yeh<sup>7</sup> used aqueous  $\text{NH}_3$  to remove  $\text{CO}_2$

from simulated flue gas. The reaction products were analyzed by X-ray diffraction (XRD) and scanning electron microscopy. The experimental data were compared with standard data and the products identified as ABC. These methods for ABC determination are only qualitative; there is no standard quantitative method. Further, the analysis of mixtures of ABC with other ammonium salts is very challenging.

In this study, four techniques were used to determine ABC in the reaction products: FT-IR and XRD as qualitative methods and C–H–N elemental analysis and NIR spectroscopy as quantitative methods. Comparisons among these techniques are discussed.

## EXPERIMENTAL SECTION

**Materials.** Ammonium bicarbonate, ammonium carbonate, and ammonium carbamate were purchased from Aldrich, Acros Organics, and Alfa Aesar, respectively. Concentrated ammonia was purchased from Fisher Scientific and diluted with 18 M $\Omega$ ·cm water from a Nanopure system. Simulated flue gas (14.7% carbon dioxide, balance nitrogen) was purchased from Airgas.

**Experimental Bench-Scale  $\text{CO}_2$  Capture System.** A schematic diagram of the experimental system for studying the removal of  $\text{CO}_2$  gas by ammonium scrubbing is shown in Figure 1. The  $\text{CO}_2$  scrubber was a glass container (i.d. 50 mm) filled with 150 mL of 15%  $\text{NH}_3$  solution. A mass flow controller was used to control the inlet flow rate at 3 L/min, and a magnetic stirrer was used to help the reactants mix well. A filter was placed after the scrubber to capture escaped particles. A photoacoustic multigas analyzer (Innova 1312) was used for monitoring the outlet  $\text{CO}_2$  and  $\text{NH}_3$  concentrations. Experiments were conducted at room temperature ( $25 \pm 1$  °C).

**FT-IR Analysis.** The reference compounds were mixed with KBr to form a uniform mixture and compressed to formed pellets. The pellets were scanned using a Perkin-Elmer 1600 FT-IR instrument from 450 to 4400  $\text{cm}^{-1}$  with 2- $\text{cm}^{-1}$  resolution.

**XRD Analysis.** A Thermo ARL X'TRA X-ray diffractometer with Cu K $\alpha$ 1 radiation ( $\lambda = 1.540\,562$  Å, 45 kV, and 40 mA) was used for the XRD analyses. The step size was 0.04°, and diffraction patterns were recorded in the  $2\theta$  range 10–60°.

**Carbon–Hydrogen–Nitrogen Elemental Analysis.** A Leco CHN-2000 was used for elemental analyses. Forty-milligram samples are combusted in the furnace with oxygen gas and the carbon, hydrogen, and nitrogen are converted into  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , and  $\text{NO}_x$ . An aliquot of the combustion gases passes through infrared cells to determine the carbon and hydrogen content. The  $\text{NO}_x$  in the combustion gases is reduced to  $\text{N}_2$ , and a thermal conductivity cell determines the nitrogen.

**NIR Spectroscopy.** A Brimrose Luminar 4030 Miniature Free Space Process NIR analyzer with acoustooptical tunable filter (AOTF) optics was used over the wavelength range of 1100–2300 nm with 2-nm resolution. The Camo Unscrambler chemometrics software package was used to analyze the NIR data.

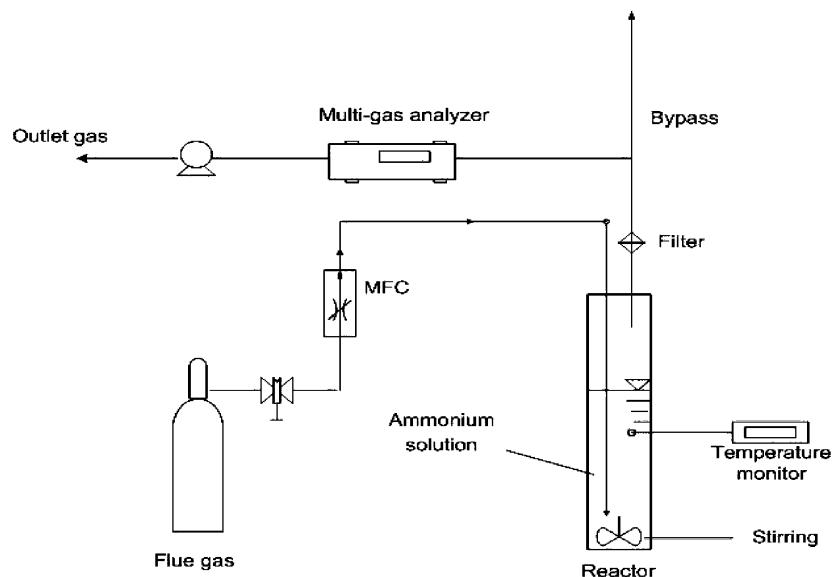
## RESULTS AND DISCUSSION

**FT-IR Analysis.** Figure 2 shows the FT-IR spectra of the three standards. In ABC's spectrum, the peaks in the region of 1200–1450  $\text{cm}^{-1}$  are the asymmetric CO stretch of the bicarbonate ion, and the peak at  $\sim 1600$   $\text{cm}^{-1}$  is the symmetric CO stretch. In the spectrum of ACN, the peaks in the region 1300–1600  $\text{cm}^{-1}$  are the asymmetric CO stretch of the carbonate ion. The spectra of

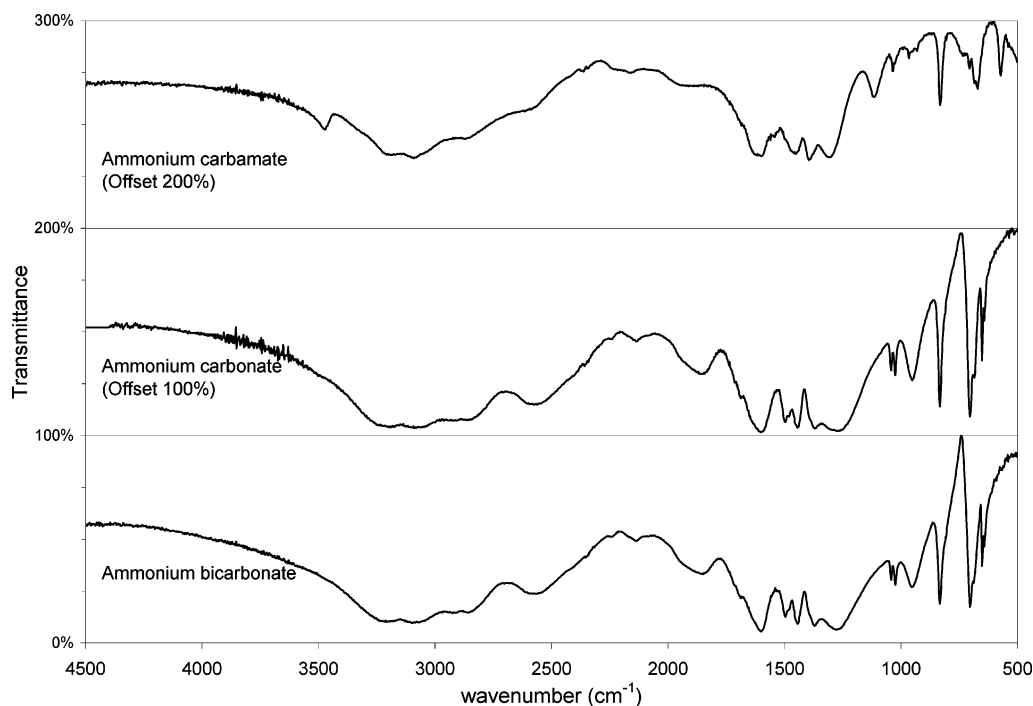
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**Figure 1.** Schematic diagram of the bench-scale CO<sub>2</sub> scrubber.



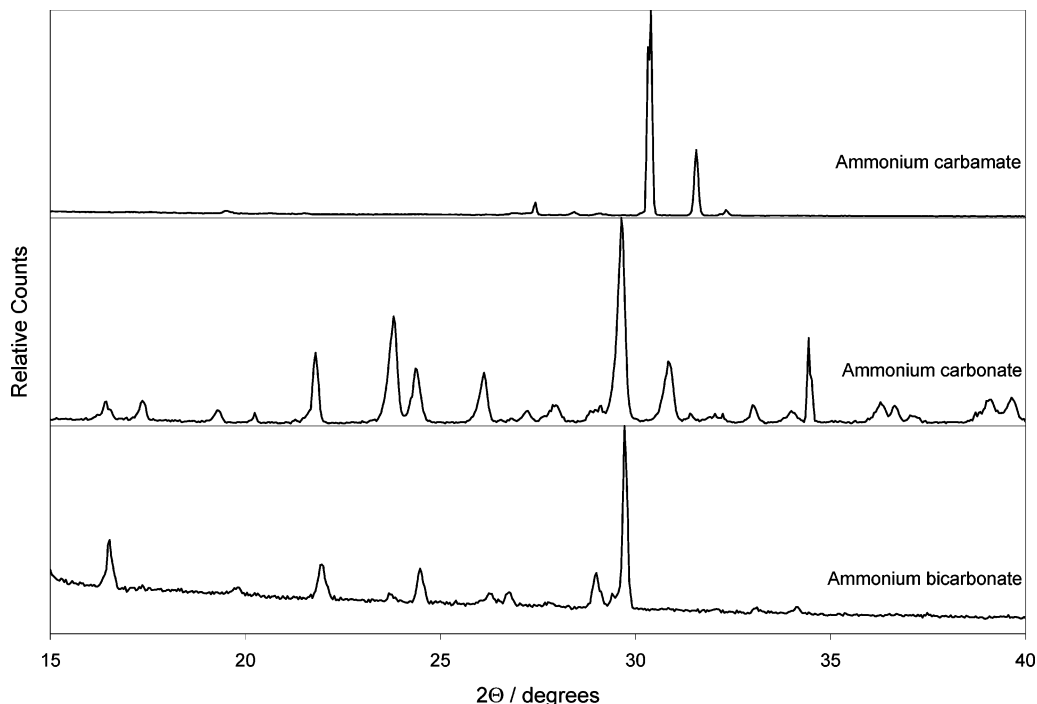
**Figure 2.** FT-IR spectra of ABC, ACN, and ACM standards.

ABC and ACN are quite similar and difficult to distinguish because of broad peaks due to both carbonate and bicarbonate between 1200 and 1700 cm<sup>-1</sup> and the same peak at 3098 cm<sup>-1</sup>, which is due to the ammonium ion. However, the peak at 3472 cm<sup>-1</sup> in the spectrum of ACM, which is due to NH<sub>2</sub>, is not found in the spectra of ABC or ACN. This shows that FT-IR can only be used to distinguish ACM from ABC and ACN, but not ABC from ACN.

**XRD Analysis.** The three ammonium salts are all white crystalline solids. Their XRD patterns could provide some information for differentiating ABC from the other products. Figure 3 shows the XRD spectra of the three standards. Table 1 summarizes the three most intense XRD peaks and their relative intensities for each of the three compounds. Unlike the FT-IR

spectra, obvious differences are found among the XRD patterns of these three compounds. The peak at  $2\theta$  of 16.5 in the XRD spectrum of ABC and the peak at  $2\theta$  of 34.4 in the XRD spectrum of ACN are unique to each of the compounds, which indicates XRD can differentiate ABC from the other possible products of the CO<sub>2</sub> capture reaction. Thus, in this application, XRD was used only as a qualitative technique for analyzing the scrubber products. XRD spectra indicate that the main product of the scrubber system has high concentrations of ABC, which were quantified by CHN elemental analyses and NIR techniques (vide infra).

**CHN Elemental Analysis.** Carbon, hydrogen, nitrogen, and oxygen are the only elements in the reaction products. Because there are stoichiometric relations among these compounds,



**Figure 3.** XRD spectra of ABC, ACN, and ACM standards. The baseline of each spectrum is zero counts for that spectrum, and all are normalized to their most intense peak.

quantitative analysis of the ABC in the reaction products by CHN elemental analysis is possible. According to eqs 7 and 8, the only products under the controlled conditions are ABC and ACN.

The composition of the reaction products can be determined using a system of simultaneous equations with the symbols defined as follows:  $X$  is the mass percentage of ABC (MW 79.06) in the reaction products;  $Y$  is the mass percentage of ACN (MW 96.09) in the reaction products;  $C$  is the mass percentage of carbon (MW 12.01) as determined by elemental analysis;  $N$  is the mass percentage of nitrogen (MW 14.01) as determined by elemental analysis.

The two equations are

$$C = \frac{12.01}{79.06}X + \frac{12.01}{96.09}Y \quad (9)$$

$$N = \frac{14.01}{79.06}X + \frac{28.02}{96.09}Y \quad (10)$$

Solving for  $X$  and  $Y$  from eqs 9 and 10 gives

$$X = 79.06 \left( \frac{2C}{12.01} - \frac{N}{14.01} \right) \quad (11)$$

$$Y = 96.09 \left( \frac{N}{14.01} - \frac{C}{12.01} \right) \quad (12)$$

Quantitative results of these analyses for two representative samples from the bench scale scrubber are shown in Table 2. These results show that the ABC assay of samples 1 and 2 is above 97% and confirm that ABC is successfully produced by the scrubber. The results for percent ABC in samples 1 and 2 have standard deviations of 0.53 and 0.29, respectively, which indicates this determination has good reproducibility. While using an

**Table 1. XRD Summary Data (Wavelength 1.540 56 Å)**

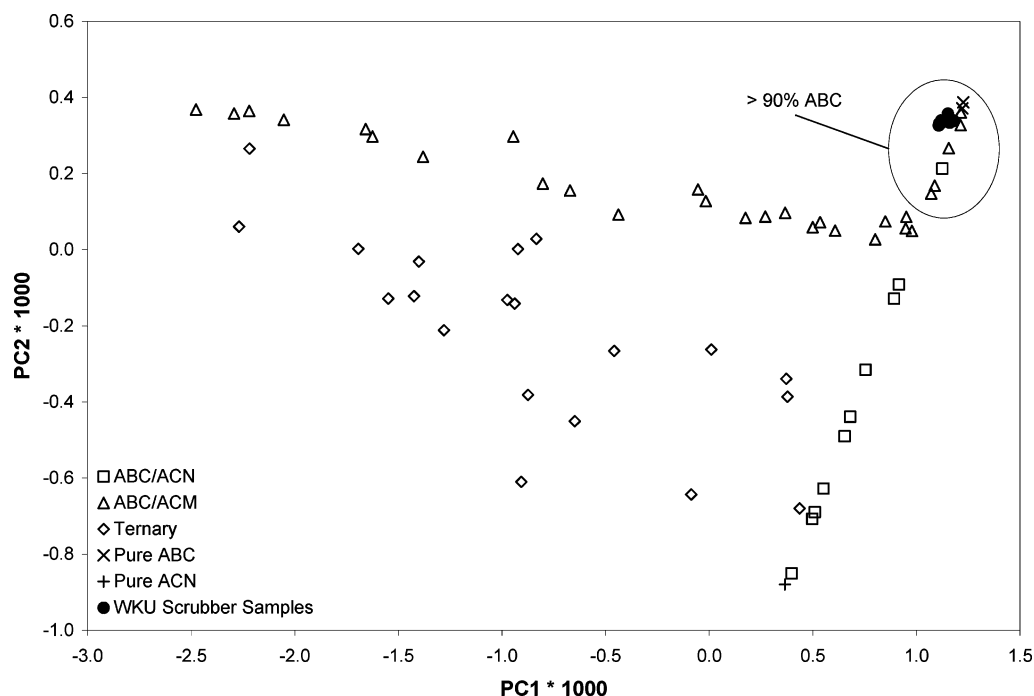
standard	$2\theta$ (deg)	$d$ spacing (Å)	relative intensity (%)
ammonium bicarbonate $\text{NH}_4\text{HCO}_3$	29.7	3.00	100.0
	16.5	5.36	26.5
	22.0	4.04	19.4
ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$	29.6	3.01	100.0
	23.4	3.74	49.7
	34.4	2.60	42.8
ammonium carbamate $\text{NH}_2\text{CO}_2\text{NH}_4$	30.4	2.94	100.0
	31.5	2.83	32.0
	27.4	3.25	6.0

**Table 2. Quantitative Results of the CHN Elemental Analysis for Two Samples from the Bench-Scale Scrubber System**

sample ID	% C	%H	% N	% ABC	average %ABC	standard deviation
1	15.09	6.257	17.76	98.36	98.00	0.53
	15.00	6.202	17.69	97.68		
	15.11	6.248	17.78	98.52		
	14.94	6.158	17.59	97.42		
2	15.03	6.222	17.82	97.25	97.61	0.29
	15.09	6.218	17.90	97.66		
	15.07	6.245	17.86	97.59		
	15.11	6.258	17.89	97.95		

instrument such as the Leco CHN-2000 to determine the composition of the reaction products is accurate and relatively fast, this technique is not an ideal tool for the on-line determination of ABC in a full-scale scrubber setting.

**NIR Spectroscopy.** The bicarbonate ion has one oxygen–hydrogen bond not present in the carbonate or the carbamate, which results in a NIR peak at ~1450 nm. Initially, a suite of 63



**Figure 4.** Scores plot of the PCA.

mixtures of the ammonium compounds was prepared. These mixtures fell into three groups: ABC–ACN mixtures, ABC–ACM mixtures, and ternary mixtures, all in varying percentages by mass. The second-derivative spectra (between 1400 and 1550 nm) of these samples were analyzed using a principal components analysis (PCA). This narrow wavelength range allows for a very fast analysis with the AOTF optics used in the Brimrose spectrometer. The spectra of all the mixtures were free of noise in this region and have sufficient spectral variation with which to perform a multivariate analysis as shown by the results of the PCA. In fact, Figure 4 reporting the scores plot of the PCA indicates that samples with a high percentage of the ABC (>90% as indicated) are grouped together and are not dependent on the remaining composition of the sample. However, as the percentage of ACN or ACM is increased, the samples separate into two additional groups. The primary region of interest is where the standard samples are similar to the test samples, >90% ABC. In this area of PC space, the PCA cannot distinguish between ABC–ACN and ABC–ACM samples because ABC dominates the spectra. The first principal component describes 81% of the total variance and the second 14% of the total variance.

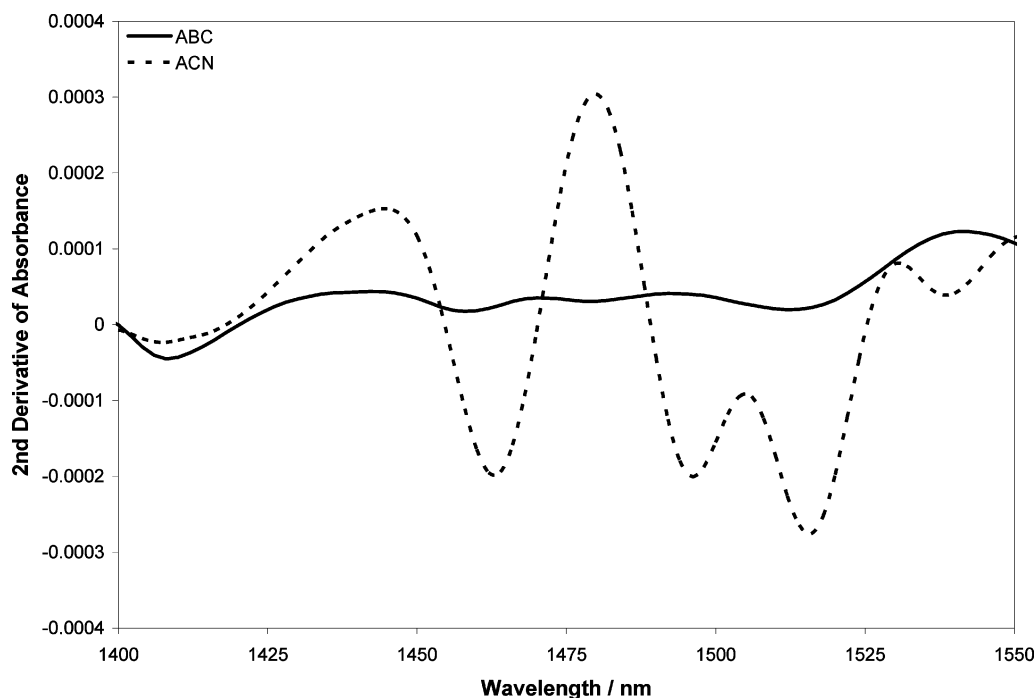
The spectra and the composition data were used to perform a partial least-squares (PLS) regression with the constituent of interest being ABC. The PLS regression used three latent variables to explain 100% of both the spectral and constituent variations for ABC. The calibration yielded a slope of 0.97, a correlation of 0.99, a standard error of calibration (SEC) of 4.1%, and a bias of <0.1%. The cross validation yielded a slope of 0.97, a correlation of 0.98, a standard error of prediction (SEP) of 4.7%, and a bias of <0.1%. This regression model for percent ABC indicates a strong correlation between the spectral data and reference composition values. The slope and bias for both calibration and cross validation are almost ideal, translating into an accurate quantitative model from 0 to 100% ABC. The predicted versus measured plot for the cross validation is almost identical to that for the calibration. This

indicates the model is indeed robust, using only three latent variables to explain all the variation between samples. The residuals for both calibration and cross validation are small and indicate that a precise model can be translated into an on-line analysis system.

In Figure 4 it can be seen that the data points for ABC–ACN mixtures lie along a straight line from pure ACN to pure ABC. The linear least-squares correlation coefficient between PC1 and the percentage of ABC is 0.976. In fact, the same correlation coefficient is found between PC2 and percent ABC for these mixtures. Since the products of the scrubbing system are expected to include only ABC and ACN, an additional suite of 81 mixtures of only ABC and ACN was prepared and analyzed by NIR. Figure 5 shows the second-derivative spectra of the ABC and ACN standards in the range from 1400 to 1550 nm. The second-derivative NIR spectra and the composition data for these 81 samples were used to generate a PLS regression model that employed two latent variables to explain 100% of the spectral and 96% of the constituent variation for ABC. The calibration for this refined PLS yielded a slope of 0.97, a correlation of 0.99, a SEC of 3.8%, and a bias of <0.1%. The cross validation for this refined PLS yielded a slope of 0.98, a correlation of 0.98, a SEP of 4.1%, and a bias of <0.1%. The predicted versus measured plot for cross validation of this PLS is again almost identical to the calibration plot, indicating a robust model.

This PLS regression model was used to predict the percentage of ABC in 13 test samples from the bench-scale scrubber, giving close agreement with the separate determination of the ABC by CHN elemental analysis. The RSD in the percentage of ABC for the test samples ranged from 0.17 to 2.59%. Table 3 shows the results of predictions using the refined PLS model and the validated results from the CHN elemental analysis on 13 samples from the bench-scale scrubber. When comparing the NIR results with the results from the CHN elemental analysis, we find the ABC contents in samples 1–8 are very close, with differences





**Figure 5.** Second derivative of NIR spectra for ABC and ACN.

**Table 3. Summary Data for the 13 Samples from the Bench-Scale Scrubber System**

sample ID	% ABC by NIR <sup>a</sup>	% ABC by CHN <sup>a</sup>	% difference NIR vs CHN
1	98.36 (0.17)	98.00 (0.53)	0.37
2	95.64 (0.26)	97.61 (0.29)	-2.02
3	96.22 (0.46)	97.66 (1.02)	-1.47
4	93.42 (0.19)	97.89 (0.37)	-4.57
5	90.72 (1.33)	92.80 (2.91)	-2.24
6	85.81 (0.36)	89.87 (2.57)	-4.52
7	92.92 (1.10)	91.22 (1.04)	1.86
8	96.53 (0.86)	98.43 (1.10)	-1.93
9	87.93 (0.34)	99.45 (0.48)	-11.6
10	89.88 (0.47)	98.13 (1.36)	-8.41
11	88.32 (0.21)	97.38 (0.29)	-9.30
12	57.74 (0.69)	96.92 (0.56)	-40.4
13	65.75 (1.70)	97.26 (0.77)	-32.4

<sup>a</sup> Standard deviations in parentheses.

below 5%. Both the CHN and NIR methods indicate the ABC assay of samples 1–11 is above 85%. Samples 12 and 13 have a large uncertainty, primarily due to the particle size and small amount of sample available for NIR analysis.

Since this model uses only 150 wavelengths, the method of analysis is extremely efficient; a typical analysis would only take ~1 s to produce reasonably accurate and precise results. If increased accuracy is needed, the number of scans per sample can be increased without increasing the scanning time substantially. This makes an AOTF-based NIR spectrometer an ideal tool for creating an on-line measurement system for ABC in the

products of an aqueous ammonia CO<sub>2</sub> scrubber. The AOTF technology allows for fast scanning with no moving parts and without the need to recalibrate the system. A free space spectrometer can be mounted in the reaction product recovery system, and noncontact classification analysis can be performed. The spectrometer can send a signal to the process control system indicating the results of the determination, which can be used to tune the performance of both the combustion and scrubbing systems.

## CONCLUSION

Various analytical techniques were used to determine ABC in the products of a bench-scale aqueous ammonia CO<sub>2</sub> scrubbing system. FT-IR and XRD were used to qualitatively distinguish ABC from ACN and ACM. CHN elemental analysis and NIR spectroscopy were used to quantify the ABC and show that an AOTF-based NIR spectrometer is an ideal tool for on-line measurement of ABC because this technology allows for fast scanning with no moving parts and is without the need to recalibrate the system.

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