Real-Time Process Monitoring of CO_2 Capture by Aqueous AMP-PZ Using Chemometrics: Pilot Plant Demonstration

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S *Supporting Information*

ABSTRACT: A combination of analytical instrumentation and multivariate statistics is widely applied to improve in-line process monitoring. Currently, postcombustion CO_2 capture (PCC) technology often involves the use of multiamine based chemical reagents for carbon dioxide removal from flue gas. The CO_2 capture efficiency and overall process performance may be improved by introduction of the chemometrics analytical methods for flexible and reliable process monitoring. In this study, six variables were measured (conductivity, pH, density, speed of sound, refractive index, and near-infrared absorbance spectra). A compact data-collecting chemometric setup was constructed and installed at an industrial pilot plant for real-case testing. This setup was applied to the characterization of CO_2 absorption into aqueous 2-amino-2-methyl-1-propanol (AMP) activated by piperazine (PZ) as the absorption agent. A partial least-squares (PLS) regression model was calibrated and validated based on the measurements conducted in the laboratory environment. The developed approach was applied to predict the concentrations of AMP, PZ, and CO_2 with accuracies of ±2.1%, ± 3.5%, and ±4.3%, respectively. The model was constructed to include the temperature dependency in order to make it insensitive to operational temperature fluctuations during a CO_2 capture process. The setup and model have been tested for almost 850 hours of in-line measurements at a postcombustion CO_2 capture pilot plant. To provide validation of the chemometrics approach, an off-line analysis of the samples has been conducted. The results of the validation technique benchmarking appear to be consistent with values predicted in-line, with average deviations of ±1.8%, ± 1.3%, and ±3.9% for the concentrations of AMP, PZ, and CO_2, respectively.

INTRODUCTION

The operation and monitoring of chemical processes requires reliable methods for continuous online control of running processes, determination of properties of liquids and gases, and determination of the response to changes in the process conditions.[1−4] One of the industrial processes that is receiving a lot of attention lately is postcombustion CO_2 capture (PCC), a technology aimed to reduce the carbon dioxide emissions to the atmosphere caused by the electric power industry, chemical industry, and heavy industry.[5−7] Chemical absorption is the current standard for PCC from power plants using amine-based solvents as the chemical absorption agent.[8−11] Counter-current flows of the amine-based solvent and the exhaust stream are brought into contact inside an absorber column, thus removing carbon dioxide from the flue gas. The resulting CO_2-rich liquid solvent is pumped toward the thermal desorption column, where CO_2 gas is released from the solvent due to increased temperature. The regenerated CO_2-lean solvent is supplied back to the absorber column. The water−amine ratio is subject to change due to the emissions of the solvent in the absorption−desorption system, flue gas composition, gas/liquid flow rate, and solvent degradation phenomena.[12−14] Hence, the CO_2 capture rate also changes in time. Continuous monitoring of the composition of the solvent stream is advantageous, since

it provides fast feedback in response to changing process conditions.

It is common practice to analyze solvent streams off-line by taking a sample from the lean and rich streams of the capture plant and performing, for instance, Fourier Transform Infrared (FTIR) spectroscopy analysis[15] or more expensive LC-MS tests[16] to determine the composition of the liquid solvent. Accurate multicomponent system characterization is one of the main goals for informative process analysis.[17] It is especially important when substances in a mixture are hard to distinguish from one another (mixtures of two and more amines), but their concentrations have an impact on the overall performance of the process. So called "at-line" analysis, using instruments placed close to the process line, requires sample transportation and poses risks of sample contamination during tests.[18] Direct in-line installation of monitoring tools for analysis of both the lean and rich solvent slip streams reduces the likelihood of external influences and increases the flexibility of the industrial process control. From this perspective, the combination of the

multivariate measurements with subsequent data extraction using statistical tools and computer programming (chemometrics) has proven to be a powerful approach for the construction of descriptive and predictive models for chemical systems.[19−22]

Recently, a similar chemometrics approach has been successfully implemented for in-line monitoring of monoethanolamine (MEA) and absorbed CO_2 concentrations.[23] Another work presented the statistical data processing of the Attenuated Total Reflection FTIR (ATR FTIR) spectral responses to analyze a solvent composed of neutralized β-Alanine as a capture agent for CO_2 absorption.[24] The models were built to predict the concentrations of the acid gas (CO_2) and capture agent. The predictions were restricted to a single operational temperature, which suggests frontiers for improvements in the flexibility.

This study focuses on three-component mixture analysis. A solvent blend of aqueous 2-amino-2-methyl-1-propanol (AMP) activated by piperazine (PZ) and loaded with CO_2 was studied in a laboratory and also monitored at an industrial pilot plant. The AMP−PZ solvent blend is reported to be an energy and material saving alternative to conventional MEA-based solvents for the PCC process.[25,26] In the current work, the application of the in-line chemometrics approach for the discrimination between the two amines that make up the solvent is described. The following solvent properties were measured: density (ρ), conductivity (Ω^{-1}), pH, sound velocity (SV), refractive index (n_D), and near-infrared (NIR) absorption. A model based on the partial least-squares (PLS) regression algorithm was used for prediction of the concentrations from the set of measured data. The temperature dependency was included in the model by using the calibration data set of the measurements conducted at three temperatures: 25, 35, 40 °C. This study contains a description of the screening experiments, calibration and validation measurements, and chemometric model construction. The confirmation of the applicability of the method via testing at an industrial pilot plant with subsequent validation is presented as well. The developed approach is suitable for applications at chemical processes similar to PCC, like natural-gas treatment.

■ APPROACH

The measured physical properties of the liquids in this study are known to be highly dependent on temperature.[27,28] If the prediction ability of a chemometric model is restricted to one operational temperature, then its applicability will be too limited, since industrial processes may run at different conditions with various temperature fluctuations. The physical parameters (in this paper referring to the set ρ, Ω^{-1}, pH, SV, n_D) alone may not be sufficient for accurate model construction. Spectroscopy data of the NIR absorbance can significantly supplement the data obtained by the measurements of the physical parameters. However, the spectroscopic signal is also known to be temperature dependent, though not to such an extent as the physical parameters.[29] The calibration database for the model construction consisted of the measurements conducted at 25, 35, and 40 °C, thus containing information on the temperature dependency of every measured variable.

The range of applicability for the model was defined in accordance with the requirements of the carbon dioxide capture process. Five levels of concentrations were selected for every

compound. Each sample in the calibration set was composed of a combination of the concentrations from Table 1.

Table 1. Levels of Concentration Used for the Calibration Set[a]

	Low		Base		High
AMP [mol/kg]	2.00	2.50	3.00	3.25	3.50
PZ [mol/kg]	1.00	1.25	1.50	1.75	2.00
CO_2 [mol_{CO_2}/mol_{Amine}]	0.00	0.10	0.20	0.35	0.50

[a]Low and High are the lower and upper limits of concentrations that may be encountered during a PCC operation process; Base defines the desired process concentrations. Extra levels of concentrations were added to the calibration procedure in order to increase the resolution of the prediction model.

Given that the total number of permutations will make up 5^3 = 125 samples, the calibration procedure would become very labor-intensive, especially taking into account the number of properties that have to be measured and repeated every time for each of the three different temperatures. Therefore, a fractional factorial design of three factors at five levels was generated using the so-called 5**(3-1) approach.[30] Extra samples were mixed, in order to obtain an equally spaced array of concentrations for accurate assessment of the relations between the three compounds.

Overall, 53 samples were prepared with various concentrations of both amines and CO_2 (see Figure 1). It turned out
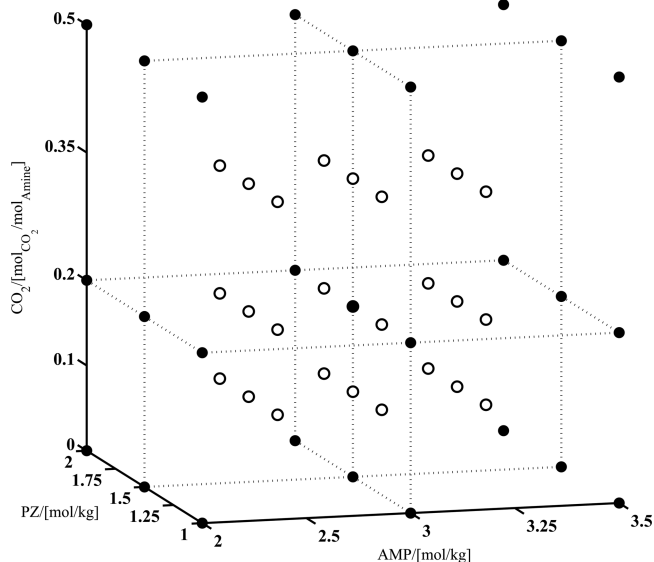

Figure 1. Graphical representation of the composition matrix of the calibration samples. The filled circles represent the training compositions for the PLS model, and the empty circles represent the compositions that serve for model testing. During the measurement campaign at the pilot plant, the whole set of samples was used as a calibration database for the PLS model.

that 12 samples were unusable because of precipitation of amine within the selected experimental temperature range. The final calibration set of samples was subjected to analysis using measurements of six variables: density (ρ), conductivity (Ω^{-1}), pH, sound velocity (SV), refractive index (n_D), and NIR absorbance. It is convenient to sort all of the measured values

into two sets of data: physical parameters and spectroscopic data.

Two separate stock solutions of aqueous AMP and PZ with CO_2 contents of 0.62 and 0.86 mol_{CO_2}/mol_{Amine} were prepared. The calibration set of samples was then prepared using certain amounts of liquid from each of the stock solutions with subsequent addition of pure AMP, PZ, and water. The final total volume of every sample was 100 mL. It is always possible to extend the model's applicability using the described samples screening procedure. Whenever the operational temperature is outside the calibration boundaries, or the composition of the liquid is not covered by the existing model, the extra measurements obtained in a laboratory might be added into the calibration database.

■ MATERIALS AND EXPERIMENTAL PROCEDURE

Chemicals. AMP (≥99%) and PZ (≥99%) were purchased from Sigma-Aldrich and used as received without further purification. Aqueous solutions of amines were prepared by mixing with deionized water at the needed proportions. Compressed CO_2 from a gas cylinder (≥99%) was used to load the stock solutions.

Measurement Instrumentation. The results of the laboratory measurements of the calibration samples were the basis for the chemometric model. The model for in-line assessment of the solvent composition was completely based on the values obtained from the calibration measurements. The construction of the in-line chemometric setup involved the measurement devices being built into the flow-through cells. Some of the laboratory measurements were performed using more suitable equipment for the generation of the calibration data. Every instrument was carefully calibrated every time before making a series of measurements with the calibration samples in the laboratory and before starting up data logging with the chemometric setup installed at a pilot plant.

Near-Infrared Spectroscopy. The NIR spectroscopy absorption signal was collected using a flow-through cell with a 5 mm path length equipped with fiber-optic cables carrying the light from the output of a tungsten halogen light source (AvaLight-HAL) to the streaming liquid and bringing the signal to the spectrometer. The same equipment was used for laboratory measurements as well as for in-line solvent monitoring. The spectrometer, light source, and software were supplied by Avantes. The wavelength range was within 1017−2044 nm with a spectral resolution of about 4 nm. The spectra acquisition time was between 3 and 4.5 ms and the averaging was done over 100−200 scans. A reference spectrum was collected from deionized water. Prior to every new measurement campaign, the reference and dark spectra were recorded again, to keep the instrument calibration updated.

Refractometry. The refractive index of the studied solutions was measured by an in-line refractometer, CM780N manufactured by Atago, calibrated in Brix % units with an accuracy of ±0.2%. The units of Brix represent the weight percentage of sucrose dissolved in pure water. The conversion of the Brix scale to n_D was performed using the empirical correlation that was provided by Atago:

$$n_D = 1.333 + Brix \cdot 1.335 \times 10^{-3} + Brix^2 \cdot 7.608 \times 10^{-6} \tag{1}$$

Sound Velocity Probe. An immersion sensor for sound velocity measurements, Liquisonic 40-40 from SensoTech,

dipped into a custom-made flow-through cell was used to acquire values of the speed of sound in the liquid. The studied liquid fills a gap between a piezoelectric ultrasonic-sound transmitter and a receiver separated from each other at a well-known distance. The measurement accuracy of the probe is ±0.01%.

Density Measurements. The density was measured by means of (a) an Elite MicroMotion Coriolis flow meter (also capable of measuring solvent mass flow), installed inside the mobile chemometrics setup, with an accuracy of ±0.05% and (b) a DMA 4500 Anton Paar U-tube density meter during measurements in the laboratory with an accuracy of ±0.005%.

pH and Conductivity Sensors. For in-line measurements, the pH readings were obtained by a pH3630 device with a 2-wire pH transmitter and the conductivity was measured by a C7635 device equipped with a 7-wire transmitter with an accuracy for both devices of ±0.1%. Both devices were obtained from Nieuwkoop B.V. The laboratory calibrations were carried out with a portable HQ11d pH meter equipped with an IntelliCAL pHC101 electrode with an accuracy of ±0.1% of value. The conductivity of the calibration samples was measured with an Orion Star A322 meter with an Orion 013010 MD conductivity cell (accuracy is ±0.5% of value), both from ThermoScientific.

Hot Phosphoric Acid Method. In order to determine the CO_2 concentration, the boiling phosphoric acid method was used. A known amount of a CO_2-loaded liquid sample was injected into a round-bottom flask with a boiling aqueous solution of H_3PO_4 (≥85%, Sigma-Aldrich). The released CO_2 was dragged away from the flask with a constant rate by the flow of N_2. Then, the gas flow was fed into a Binos 100 2M carbon dioxide analyzer from Rosemount Analytical. The CO_2 amount was automatically logged. The calibration of the method was done routinely with a 1 M solution of K_2CO_3. The accuracy of this method has been calculated to be ±4.1%.

LC-MS Measurements. The concentrations of AMP and PZ in the validation samples from a pilot plant were also measured by an LC-MS technique. The samples were diluted to 1:10 000 in water. A deuterated internal standard was added to the diluted samples for both of the analytes. The samples were analyzed with an Agilent Infinity 1290 LC-system, combined with a 6490 Triple quadrupole MS. The samples were run in MS-MS-mode. The method calibration curves for both AMP and PZ show an R^2 value >0.99.

Installation at a Pilot Plant. The solvent flow was monitored at the PCC pilot plant installed at the EnBW coal-fired power plant in Heilbronn. This pilot plant has already been used for CO_2 capture with aqueous 30 wt% MEA solution for almost 1600 operating hours.[31] Authors report that during this campaign CO_2 loadings of the solvent were above 0.5 mol_{CO_2}/mol_{MEA}. It also has been shown that solvent degradation has happened primarily due to the oxidation mechanism via formation of formate and oxalate. In order to be able to reclaim degraded solvent the electrodialysis technology was tested at the PCC pilot plant. The effective removal of heat-stable salt anions from the solvent stream has been demonstrated.[32] The PCC plant receives the flue gas and steam from the seventh unit of the power station. The flue gas volume flow was approximately 1500 Nm^3/h and the CO_2 capture rate was around 90%. The initial composition of the aqueous solvent was 3.0 M of AMP and 1.5 M of PZ. The solvent circulation rate in the system of the PCC pilot plant was in the

range of 3−6 m³/h. The height of the absorber and stripper column is 38 and 30 m, respectively. The total solvent composition is constant in the closed circulation line of the PCC pilot plant. Due to the specifications of the measurement devices, high solvent temperature becomes a limiting factor for the chemometric setup applicability. Since the temperature of the liquid in the outlet of the stripper section may reach 90 °C, it was decided to make an installation of the setup at the point where the operating temperature is lower. The solvent for in-line analysis was taken via a bypass from the intercooling section of the absorber at a rate of around 20 L/h. After flowing through the chemometric setup, it was fed back to the absorber sump (see Figure 2).
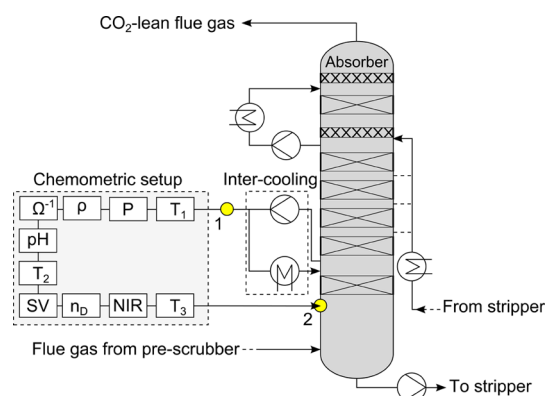

Figure 2. Schematic representation of the chemometric setup at the pilot plant. The solvent supply was provided via a bypass from the absorber's intercooling system between points 1 and 2, which are connected to the inlet and outlet of the setup. The setup consists of the following instruments: pressure sensor (P), Coriolis flow and density meter (ρ), conductivity probe (Ω^{-1}), pH probe, sonic velocity sensor (SV), refractometer (n_D), near-infrared spectrometer (NIR), thermocouples for temperature measurements at the inlet, near the center, and at the outlet of the chemometric setup ($T_{1,2,3}$).

Approximately 5 weeks of in-line solvent monitoring was conducted accompanied by data collection and analysis. The PCC pilot plant was operating mostly during day time when the steam supply from the power plant was available. At night time, the solvent was only circulating, without any flue gas and without heating in the reboiler. The plant was shut down completely during weekends. The concentrations prediction was performed using data collected at the moments when the temperature of the solvent flow was within the calibration limits.

■ DATA PROCESSING

Analytical Model Calibration and Validation. The main functionality of chemometrics in connection with process control is its ability to provide an operator with maximally relevant information about running chemical processes and to reduce the time needed for the analysis. For this purpose, the calibration measurements were conducted in order to obtain enough experimental data points to be able to construct a correlation between two sets of data: the known composition of the mixture of interest and the physical and spectroscopic responses from a set of calibration samples.

Partial least-squares (PLS) regression is a common chemometrics method.[33,34] The PLS regression models consider the correlation between the concentrations of the mixture

components and the measured responses, by constructing latent variables (LV) that directly relate to the source data. Following the recommendation, given by Wise et al.,[35] the optimal number of LVs for the PLS model was selected such that the addition of another LV does not greatly improve the accuracy of the model. The parameter for model quality assessment is the root-mean-square error of prediction (RMSEP):

$$RMSEP = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (y_{i,exp} - y_{i,model})^2} \tag{2}$$

where the values of $y_{i,exp}$ are known and the values of $y_{i,model}$ are predicted with the PLS model. The influence of the number of LVs on the RMSEP was examined using the leave-one-out method for cross-validation. Though PLS is a linear technique, it can handle even some nonlinear effects in a data set.

Two approaches have been evaluated to include temperature dependency into the chemometric model. One option is to use the Lagrange polynomial interpolation.[36] In this work, a second-order polynomial approximation of the temperature dependency was tested for each of the physical parameters and the NIR peaks. Predicting the concentrations in-line by means of such an approach for every new temperature reading coming from the industrial process requires an update of the model using the established polynomial functions for every predicting parameter.

The other approach, which is faster and avoids extra calculations, is to use all available measurements of the dependent variables at different temperatures as the source data for the model. This way the temperature dependency is already included as an inherent feature of the correlation between the source data and LVs used to build the PLS model. The final predictions represented in the section Results and Discussion of this paper were calculated using the second approach in order to introduce the temperature dependency.

NIR Spectral Data Pretreatment. It is common practice to interpret NIR spectroscopy measurements using Beer's Law,[37] which gives a linear functional relation between the amount of light absorbed by a studied sample, the distance of light travel through the sample, and the quantity of light-absorbing substance that is contained in that sample. Therefore, the raw NIR signal was first converted to the absorbance spectra using

$$A = - \log\left(\frac{I_{sample} - I_{dark}}{I_{ref} - I_{dark}}\right) \tag{3}$$

where A is the absorbance spectrum of a sample, I_{sample} is the raw NIR spectrum of a sample, and I_{ref} and I_{dark} are the reference and the dark spectra, respectively. Spectral signal windowing was performed to specify the region of the highest signal correlation with the change of the chemical composition. Subsequently, spectra were smoothed with the Savitzky−Golay algorithm.[38,39] Both the first and second derivatives of the smoothed spectra were evaluated, which results in the removal of the baseline offset differences between spectra and the differences in baseline slopes between spectra. Finally, the first derivative was selected for the PLS model construction. The automated mean-centering of all of the response factors was used as an inherent functionality built in the MatLab PLS regression algorithm.

NIR Sensitivity Assessment. The number of parameters monitored during calibration experiments and later during real case measurements was quite high, especially when considering the spectroscopy data. A spectral sensitivity analysis with respect to AMP, PZ, and CO_2 concentrations was performed in order to reduce the risks of over determination, which may happen in the case of the PLS algorithm.

It is experimentally shown that the absorption coefficient α of an electromagnetic wave in a solution is proportional to the concentration x of the absorbing substance.[40] A light absorbance may be described as follows,

$$A(\lambda, x) = \alpha(\lambda, x) \cdot l = \sum_{j=1}^{M} \alpha'_j(\lambda, x_j) \cdot x_j \cdot l = \sum_{j=1}^{M} \beta_j(\lambda, x_j) \cdot x_j \tag{4}$$

where M is a number of the chemical components in a mixture; α' is a constant coefficient, which depends on the nature of the media and the wavelength of the incident light λ; and l is the path length of the incident light.

According to eq 4, the intensity of an absorbance peak at a certain wavelength is proportional to the concentration of each solute that makes up a mixture, each with its own weighting coefficient $\beta_j(\lambda)$, which in turn may be treated as a sensitivity parameter:

$$\beta_j(\lambda) = \frac{\Delta y(\lambda)}{\Delta x_j / \overline{x}_j} \tag{5}$$

where $\Delta y(\lambda) = y(\lambda) - \overline{y}(\lambda)$ and $\Delta x_j = x_j - \overline{x}_j$ are the deviation of the intensity of an absorbance peak and of the substance's concentration from its average value, respectively.

■ RESULTS AND DISCUSSION

Chemometric Model Test and Trial. The prediction accuracy of a model is dependent on the source measurements that are used for its construction. Individual PLS models have been built and calibrated using measurements of physical and NIR responses separately as well as with the entire set of the parameters. A complete summary of the calibration sample compositions as well as measurements of the physical properties at three different temperatures may be found in the Supporting Information for this article.

Physical Parameters. The sensitivity of the measured parameters to the variation of the unknown variables (the concentrations of both amines and CO_2) was evaluated using the coefficient of determination ($0 \leq R^2 \leq 1$). The R^2 parameter indicates the predictive quality of the model fit.[30] The coefficient of determination is an important statistical method for determining the degree of linear correlation of variables. The R^2 values are calculated as the proportion between the explained variance of the observed data and the variance of these data around its mean value. In this work the R^2 values were calculated for the PLS models that were constructed based on each of the physical response factors separately, as well as on their combinations. For instance, when using only the combination of conductivity and density measurements, the concentration of CO_2 contained in the samples may be predicted quite accurately with a deviation of 4.5%. The model built on the combination of $[\Omega^{-1}, pH, SV, n_D]$ allowed for the prediction of the concentrations for AMP and CO_2, but the addition of density measurements increased the prediction quality only for CO_2 and decreased it for both

amines. The results of the sound velocity and density measurements combined together yielded the best prediction of the PZ concentration.

NIR Spectra. Figure 3 shows the sensitivities calculated according to the procedure described in the section NIR
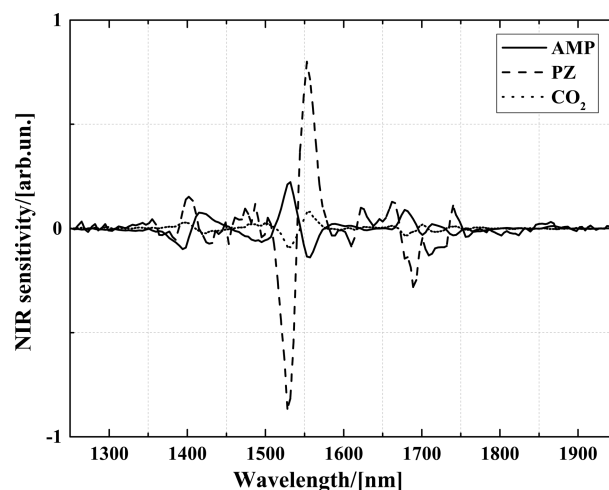

Figure 3. NIR absorbance sensitivity to the variation of the AMP, PZ, and CO_2 concentrations.

Sensitivity Assessment. This figure illustrates the significant role of NIR spectroscopy in the distinction between the two amines. The addition of spectroscopic data to the model has greatly improved the accuracy of the model in predicting the PZ concentration, decreasing the error from 7.3% to 3.5%, as shown in Table 2. Prior to the calculations, the NIR absorbance spectra may be windowed to the wavelength range from 1350 to 1750 nm without losing valuable information.

Table 2. Symmetric Mean Absolute Percentage Error (SMAPE) Calculated Based on Different Sets of PLS Model Predictors

	$SMAPE_{AMP}$	$SMAPE_{PZ}$	$SMAPE_{CO_2}$
Physical data	5.6%	7.3%	4.6%
NIR	2.1%	3.5%	7.3%
Physical and NIR data	2.1%	3.5%	4.3%

Physical and NIR Data. The physical data and NIR signal were concatenated into a single vector for every sample from the calibration data set and from every measurement during in-line monitoring. The resulting information was used as an input for PLS model construction and subsequent prediction of the concentrations in the process flow. The symmetric mean absolute percentage error (SMAPE) was calculated to assess the accuracy of the model in predicting the concentrations of both of the amines and CO_2. The SMAPE (as defined below) represents the average size of errors relative to the actual data and reduces the influence by outliers.[41]

$$SMAPE = 100 * \frac{\sum_{i=1}^{N} |y_{i,exp} - y_{i,model}|}{\sum_{i=1}^{N} (y_{i,exp} + y_{i,model})} \tag{6}$$

Table 2 shows how combinations of data sets used for model calibration influence its accuracy. Obviously, the addition of the spectroscopy measurements improved the ability of the model

in distinguishing between the two amines that compose the solvent blend. On the other hand, the physical parameters were already sufficient to predict the CO_2 concentration in a solvent.

Table 3 provides the quality of the chemical component predictions if the temperature dependency is not included as a

Table 3. Symmetric Mean Absolute Percentage Error (SMAPE) of the Predictions with the PLS Models Constructed at Separate Temperatures

T, °C	$SMAPE_{AMP}$	$SMAPE_{PZ}$	$SMAPE_{CO_2}$
25	3.8%	6.1%	6.7%
35	3.7%	7.3%	5.6%
40	3.7%	5.0%	10.6%

feature in the PLS model. Each row of Table 3 corresponds to the prediction models constructed using the source data measured at one of the following temperatures: 25, 35, and 40 °C. The optimal number of latent variables to be used by the PLS regression function for predictions was selected to be 3 for AMP, 2 for PZ, and 2 for CO_2. Such choice provided the lowest errors of prediction.

Standard error of the prediction (s_e), eq 7, is a common measure used to evaluate the errors of the statistical models such as PLS regression. The value of s_e shows that 68% of deviations fall within the limits of $\pm 1\ s_e$ for normally distributed variables.

$$ s_e = \sqrt{\frac{\sum_{i=1}^{n} \left(y_{i,exp} - y_{i,model} \right)}{(n-2)}} \qquad (7) $$

where n is the number of validation tests, $y_{i,exp}$ is a value, measured using validation methods, and $y_{i,model}$ is a predicted value.

Pilot Plant In-Line Monitoring. Real-time monitoring of a carbon capture process was carried out in-line at the PCC plant discussed in section Installation at a Pilot Plant. Continuous process data logging together with immediate remote access to the stored data has established the possibility for fast prediction of the amines and CO_2 concentrations in the solvent flow. The

temperature range for the model correction was selected based on the requirements from the PCC plant.

Since every device in the chemometric setup has its own range of applicability, within which it is calibrated, some of the data points have to be excluded from the set of predictors. For instance, if the readings from the Coriolis-flow density meter start to fluctuate outside of the calibration region, it provides an unstable signal and, as a consequence, the error of the model prediction increases. It has been observed that, during the nonoperational state of the pilot plant, the readings from the chemometric setup provide confusing source data that impair the outcome of the model. Thus, the final predictions were made using data that were collected during those hours when the pilot plant was in a state of operation. Every data point in Figure 4 represents the concentration of either AMP, PZ, or CO_2 at the corresponding moment in time. Thus, the developed measurement setup and the PLS model have demonstrated the feasibility of the chemometrics approach to in-line industrial process monitoring.

Throughout the pilot plant campaign, samples were collected for subsequent validation of the constructed model by means of off-line analytical methods. The predictions of the concentrations of AMP and PZ were validated by means of the LC-MS method. The concentration of CO_2 was measured by the hot phosphoric acid method for the model validation purpose. Demonstration of the performance of the off-line validation analytical techniques is shown in Table 4. On an average, the bias of the absolute value between the results obtained using model predictions and validation measurements is −0.05 mol/kg for the concentration of AMP and CO_2 and −0.01 mol/kg for PZ.

The last row in Table 4 contains the average deviations between the values of the concentrations calculated using the PLS model and measured by the corresponding off-line validation technique in the samples that were withdrawn at the same date and time. The average deviations were calculated in terms of SMAPE and equal to ±1.8%, ±1.3%, and ±3.9% for the concentrations of AMP, PZ, and CO_2, respectively.
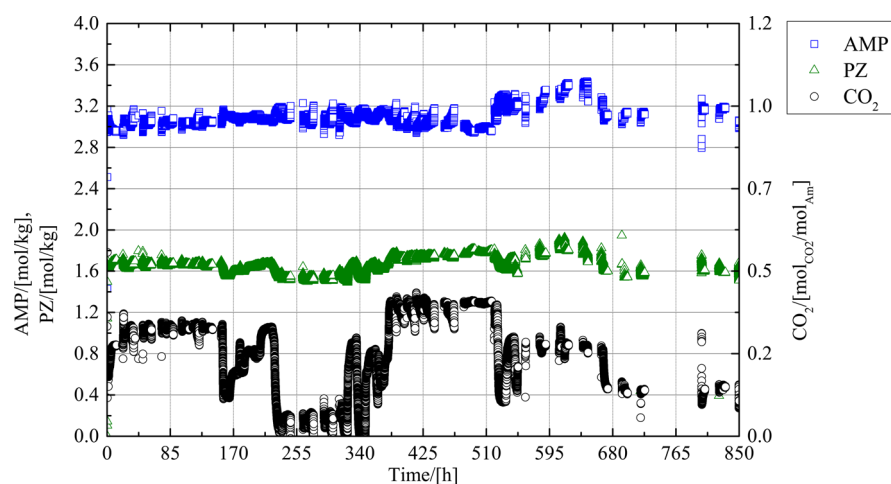

Figure 4. Predictions of the AMP, PZ, and CO_2 concentrations in the process stream during the state of operation using the PLS model, which includes the temperature dependency. Time scale represents the hours of in-line measurements starting from the beginning of the process monitoring campaign. The complete set of the measured physical parameters and NIR spectroscopic data is used for making predictions.

Table 4. Comparison of the Concentrations of Solvent Components, Calculated by the PLS Model, and Measured by the Off-Line Analytical Validation Techniques[a]

Time [h]	AMP_{PLS} [mol/kg]	AMP_{LCMS} [mol/kg]	PZ_{PLS} [mol/kg]	PZ_{LCMS} [mol/kg]	$CO_{2,PLS}$ [mol_{CO_2}/mol_{Amine}]	$CO_{2,HotH_3PO_4}$ [mol_{CO_2}/mol_{Amine}]
183	3.09	2.92	1.69	1.61	0.61	0.67
225	3.24	3.02	1.57	1.59	1.30	1.14
374	3.15	3.12	1.52	1.58	0.77	0.73
564	3.14	3.07	1.63	1.64	1.33	1.30
684	3.25	3.16	1.75	1.70	1.43	1.24
754	3.11	2.90	1.55	1.55	0.63	0.61
852	3.17	2.95	1.60	1.55	0.70	0.65
s_e	0.19		0.06		0.12	
Average deviation, ± %	1.8		1.3		3.9	

[a]The parameter s_e (standard error of prediction) is presented as a measure of the accuracy of the PLS models.

CONCLUSIONS

The current study shows the feasibility of the chemometric methods for chemical process monitoring. A complex chemometric setup was constructed and tested for in-line analysis of the multiamine-based liquid solvent used for postcombustion CO_2 capture. The operation and control of other similar industrial processes may be improved with application of the developed approach. The PLS model was created based on the measurements of density (ρ), conductivity (Ω^{-1}), sound velocity (SV), pH, refractive index (n_D), and NIR absorbance at 25, 35, and 40 °C. The model was used to predict concentrations of AMP, PZ, and CO_2 within the carbon dioxide capture process at the industrial scale postcombustion pilot plant. The concentrations of the chemical compounds were predicted with accuracies of ±2.1%, ±3.5%, and ±4.3% for AMP, PZ, and CO_2, respectively. The method has been validated by off-line analysis of the samples withdrawn during the measurement campaign. The deviation between the values predicted by the PLS model and the off-line technique remains untrended in time. A Raman spectroscopy analysis with more elaborated pretreatment of the spectral signal (indirect hard modeling, IHM[42]) may enhance the approach further via the introduction of chemical speciation of the solvent on a more detailed level. Moreover, one of the possible future developments of the above presented setup would be its miniaturization, rapid data treatment, and more user-friendly approach of the technique. This could decrease costs of the process operation by providing fast data analysis with high accuracy.

ASSOCIATED CONTENT

ⓢ Supporting Information

Complete summary of the calibration sample compositions as well as measurements of the physical properties at three different temperatures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.5b00691.

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Notes
The authors declare no competing financial interest.

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