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# Process Analytical Technology for CO<sub>2</sub> Capture

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Additional information is available at the end of the chapter

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## Abstract

Carbon capture and storage, which is also known as CCS, is an obligatory climate change mitigation technology to reduce the carbon dioxide gas emissions to the atmosphere thus limiting the average global temperature increase to 2°C. Process analytical technology is a scientific tool to improve process qualities and performance through timely measurements. This chapter describes how process analytical technology can be imbedded to a carbon capture technology by giving a detailed example of implementation of a process analyzer to CO<sub>2</sub> capture by alkanolamine absorption process. Such an implementation requires success in five elements, which are described in this chapter. They are as follows: selecting an appropriate process analyzer, integration between the analyzer and the process, model development to enable the analyzer to predict a process-related chemical or physical attribute, use of the developed model in real-time application and use of the data obtained from the analyzer as an input to a process control unit. Partial least square regression model is a useful chemometric-based method to extract hidden chemical information in measurements from a process analyzer. In this chapter, four partial least square regression models are presented, which are developed to predict CO<sub>2</sub> concentration for four different alkanolamine solutions when these amines are used to absorb CO<sub>2</sub> from a combustion process.

**Keywords:** climate change, carbon dioxide capture, process analytical technology, process analyzers, chemometrics, partial least square regression, Raman spectroscopy

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## 1. Introduction

### 1.1. Carbon dioxide and climate change

The Earth's atmosphere contains greenhouse gases such as water vapor, methane, ozone, carbon dioxide and nitrous oxide in trace levels, which have the ability to trap heat. By trapping

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heat, temperature of the atmosphere increases which is referred to *greenhouse gas effect*. The greenhouse gas effect is a naturally occurring function in the atmosphere, but when the greenhouse gas level exceeds a certain amount, it couples with the climate and changes the natural equilibrium in the environment. Climate change mitigation actions are a top priority across the world today to fight the greatest environmental threat mankind has ever faced. Carbon dioxide ( $\text{CO}_2$ ) is not the strongest greenhouse gas but among all greenhouse gases, it is the most unwanted as it has made the highest influence to the climate change during the past 270 years [1]. While promoting green technologies such as renewable energy sources to reduce and avoid  $\text{CO}_2$  emissions to the atmosphere, capturing  $\text{CO}_2$  from the current emission sources is required to reach the climate change mitigation targets such as the  $2^\circ\text{C}$  target. Major  $\text{CO}_2$  emission point sources are fossil fuel and biomass energy facilities, cement, iron & steel and petrochemical industry.

$\text{CO}_2$  capture and storage (CCS) is a three-step process consisting of  $\text{CO}_2$  capture from emission sources;  $\text{CO}_2$  transportation to storage sites and store in underground geological formations. In combustion processes,  $\text{CO}_2$  can be captured either in pre-combustion or in post-combustion mode.

## 1.2. Carbon dioxide capture technologies

$\text{CO}_2$  can be separated from flue gas or fuel gas stream by processes such as absorption, adsorption, membrane separation, chemical looping, hydrate based separation, biochemical methods and cryogenic distillation. Among these separation technologies, the absorption process is the most mature because the basic technology is well known. Typical sorbents are alkanolamines and potassium bicarbonate. The most preferred option for retrofitting existing plants is post combustion capture technology (PCC), where  $\text{CO}_2$  is scrubbed from the flue gas after combustion has taken place.

### 1.2.1. $\text{CO}_2$ capture by aqueous alkanolamine solvents

The basic reaction mechanism between  $\text{CO}_2$  and pure amines/alkanolamines is the same; hence, both compound classes can be used for  $\text{CO}_2$  capture. Although theoretically pure amine can enhance the performance of  $\text{CO}_2$  capture than aqueous amines, pure amines and even high-concentrated aqueous amine solutions show implications in plant operations. Several experiments, pilot plant tests and theoretical simulations have been carried out to investigate the optimum amine concentration for  $\text{CO}_2$  capture systems [2, 3]. Amine volatility for pure amine is, in general, higher than aqueous alkanolamine volatility. When the amine concentration is increased, amine degradation rate becomes higher [4] and the cost required for amine oxidation inhibitors is increased.  $\text{CO}_2$  capture plants using higher amine concentrations require higher reboiler duty [5] and larger water washing sections. Therefore, aqueous alkanolamine solutions are preferred than pure amines. Furthermore, aqueous alkanolamines and in particular aqueous MEA are the commercial workhorse solvents for the  $\text{CO}_2$  capture related gas sweetening industry [6].

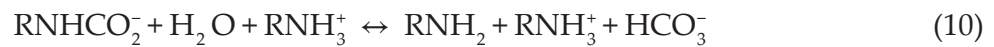
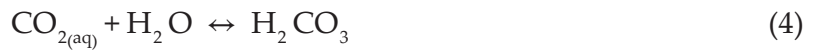
The IEA CCS road map requires to achieve 100 or more projects by 2020 to reduce the CO<sub>2</sub> capture energy penalty by 7% points by proving CO<sub>2</sub> capture technologies ready for large scale and demonstrating retrofit for 85% CO<sub>2</sub> capture [7]. The most common and cost-effective technology is absorbing CO<sub>2</sub> chemically into aqueous alkanolamine solutions such as monoethanolamine, monoethanolamine-glycol mixtures, diethanolamine, diglycolamine, diisopropanolamine, methyldiethanolamine, and mixed amines (including sterically hindered amines) [8–11]. Establishing CO<sub>2</sub> capture technology by MEA still have challenges, which have to be solved within a short period of time, such as equipment corrosion, solvent degradation, high solvent regeneration energy requirement and possible solvent emissions to the environment.

### 1.2.2. Chemical reactions of the CO<sub>2</sub>-alkanolamine-H<sub>2</sub>O system

A series of parallel equilibrium and kinetic reactions occur during CO<sub>2</sub> absorption into aqueous amine solution. This results in an electrolyte solution including ions such as OH<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, RNHCO<sub>2</sub><sup>-</sup> and RNH<sub>3</sub><sup>+</sup> as shown in reactions from Eqs. (1)–(10). Here R represents an alkyl group such as CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>. Reaction of CO<sub>2</sub> with this solution is a Brønsted acid-base neutralization reaction leading to a drop in solution pH as CO<sub>2</sub> is absorbed. The chemical composition of this solution varies according to overall solution pH.

Carbon dioxide gas physically dissolves in water to give a solvated form of carbon dioxide which is, CO<sub>2(aq)</sub> (Eq. (2)). Thereafter, CO<sub>2(aq)</sub> reacts chemically with water to give carbonic acid (Eq. (4)) which forms equilibria with bicarbonate (Eq. (5)) and carbonate (Eq. (6)) ions according to the respective pK<sub>a</sub> values. Amines are categorized as primary (RNH<sub>2</sub>), secondary (R<sub>2</sub>NH), tertiary (R<sub>3</sub>N) and sterically hindered amines (e.g., t-RNH<sub>2</sub>) based on their chemical structure. Amine reactivity of the CO<sub>2</sub>-alkanolamine-water system is determined by the N atom lone electron pair in a Zwitterion reaction mechanism [7]. Accepting a proton at the N lone electron pair, amines react as Brønsted bases according to a Brønsted acid–base reaction type. The N lone electron pair can also react with, for example, the carbon atom of the CO<sub>2</sub> molecule according to a Lewis acid-base reaction type. Carbonic acid reacts in aqueous solution with all amines in a 1:1 manner by a Brønsted acid-base reaction type to form protonated amine bicarbonate. Primary and secondary alkanolamines may also react rapidly with CO<sub>2</sub> through a Lewis acid-base reaction type to form amine carbamate. During carbamate formation, two amine molecules react with one CO<sub>2</sub> molecule; therefore, aqueous amine solutions forming protonated amine bicarbonate only achieve a higher CO<sub>2</sub> loading than aqueous primary or secondary amine solutions forming amine carbamates only.





These equilibrium equations (Eqs. (1)–(10)) can be manipulated for amine and absorbed  $\text{CO}_2$  considering the carbon and amine balance. The total number of moles of the  $\text{CO}_2$  is the sum of moles of carbonate, bicarbonate, carbamate ions and molecular  $\text{CO}_{2(\text{aq})}$ . The total number of amine moles is the sum of moles of protonated amine, free amine and carbamate ions. The mole ratio of  $\text{CO}_2$ :amine is known as  $\text{CO}_2$  loading. This value represents the  $\text{CO}_2$  absorption capacity by the amine and is considered as a crucial technology-related value. The reaction pathway for primary, secondary and tertiary amines is described in [12]. Primary and secondary amines react with  $\text{CO}_2$  to form carbamates which limits their theoretical  $\text{CO}_2$  absorption capacity to 0.5 mol  $\text{CO}_2$ /mol amine. Tertiary amines do not possess free proton in the nitrogen atom and hence do not directly react with  $\text{CO}_2$ . Their reaction pathway first involves increasing the hydroxyl ion concentration which contributes to react with  $\text{CO}_2$  to produce bicarbonate. Therefore, they have a higher theoretical  $\text{CO}_2$  absorption capacity which can go up to 1 mol  $\text{CO}_2$ /mol amine.

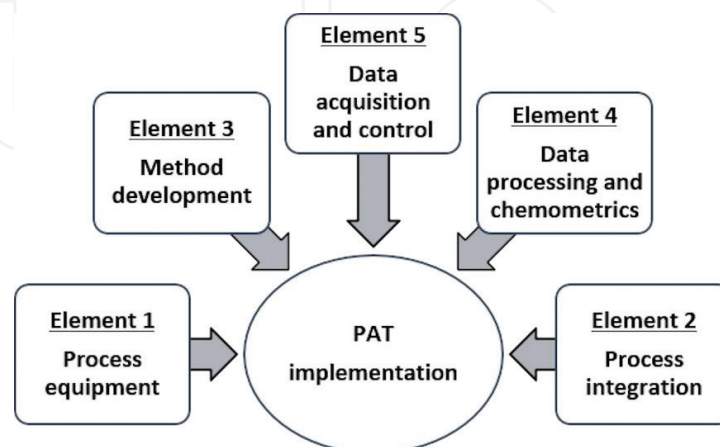
## 2. Process analytical technology and $\text{CO}_2$ capture

With reference to [13], *process analysis* is the chemical or physical analysis of materials in a process stream through in-line or on-line analyzer. *Process analyzers* can measure directly physical or chemical attributes in a system and supply data. Some key features of process analysis with respect to the laboratory analysis are: the speed of the analysis, zero manual sample handling and ability to integrate real-time data with process control. Process analytical technology (PAT) was originally defined by Food and Drug Administration (FDA) for pharmaceutical industry, as *a system for designing, analyzing, and controlling manufacturing through timely measurements (i.e., during processing) of critical quality and performance attributes*

of raw and in-process materials and processes, with the goal of ensuring final product quality [14]. However, PAT is a tool which can be applied to any process industry to increase its productivity by supplying product/process-related information real-time. Today, from laboratory to industrial scale, process analytical technology has replaced most of traditional methods to determine process-related attributes providing opportunities to understand chemical mechanisms, plant performance and optimization. CO<sub>2</sub> capturing is a continuous chemical process or a mass transfer operation where raw materials (e.g., flue gas from a power plant) are converted into a product (e.g., CO<sub>2</sub>-free-flue gas) in a process plant (e.g., absorption and desorption units). Unlike other industrial applications, CO<sub>2</sub> capturing is not an economically profitable process; instead it creates an additional burden to the economy such as increasing the cost of electricity production which creates a drawback for implementation. PAT has a considerable potential to support the strategies and methodologies to reach CCS targets. The concept of PAT within the CCS framework is not yet a well-discussed topic. However, the use of process analyzers in the CCS scientific research area has been gradually increasing during the last decade. This includes research on using different process analyzers to replace traditional laboratory methods, to understand reactions in the molecular level, and solvent selection based on spectroscopic data.

### 2.1. Implementation of a PAT tool for a CO<sub>2</sub> capture process

A successful and robust implementation of PAT is required to gain its widespread benefit to a process. It also saves money, time and resources. Since PAT applies to an entire product cycle, the implementation process should be modeled with simultaneous approach to sub-models such as business, production process, management, engineering, health-safety & environment and customer perspective. Although process analytical technologies improve the speed of the analysis, the stage of introducing such a technology requires knowledge, time and tremendous scientific work. Five elements are identified regarding to this stage and described in this section. **Figure 1** shows these five elements of a PAT implementation approach.



**Figure 1.** Elements of PAT implementation.

Element 1: Selecting a suitable process instrument for an application is challenging due to the variability of the availability. To determine a particular attribute of the process such as an analyte concentration, several simple to sophisticated measurement technologies are available. The vendors claim the general features of the instruments they sell but how deeply, accurately and precisely they response to our own application and the limitation of usage are unknown until we purchase the instrument and experience its measurements. Since PAT tools are expensive compared to traditional chemical analysis systems, the user may wish to use it for different applications. For instance, an R&D institution wants to use an analyzer to measure transparent liquid samples but later they also wish to analyze high turbid samples. An example is analysis of alkanolamine samples from an industrial CO<sub>2</sub> capture plant where samples are normally transparent when the fresh amines are used but will gradually become opaque due to thermal and oxidative degradation when the plant is operated continuously. If the user purchases an analyzer which only responses to transparent samples and is disturbed due to the fluorescence effect of turbidity in a sample, then this analyzer will stop its function when the solvent degradation starts. Therefore, if the investment requirement is to use this instrument throughout several days of plant operation, then the instrument selection becomes invalid and the whole implementation becomes unsuccessful. To avoid such disappointments in later stages of a PAT implementation, one should always thoroughly assess the selection criteria of the PAT tool. To ease this operation, the process can be started with categorizing available analyzers based on their selectivity, performance, limit of detection, complexity of usage, how it fits to the indoor and outdoor industrial environment as well as the budget. Analyzers can measure physical properties such as refractive index, thermal conductivity and viscosity. There are electrochemical analyzers measuring conductivity, pH and spectroscopic analyzers measuring concentration or any other attribute which is related to electromagnetic interaction. A detailed description about different types of process analyzers can be found in [15].

When selecting a suitable process analyzer, it becomes crucial whether the instrument can be easily integrated to the process system. Some instruments require advance mechanical modifications to the existing system or process stream in the installation process, which make them abatement only to that function. For example, if the requirement is plugging a sensor to a high-flow process stream, the engineer should assure that the plugging mechanism can withstand the maximum pressure of the system. Meanwhile, the process flow should not damage to the sensor. This kind of plugging modifications is normally fixed or permanent, and if the sensor is required to remove from the system, the process flow should be stopped and demand time. These practical problems restrict the analyzer only to this application. If we consider an insertion probe in a liquid stream, there are some critical factors affecting to the quality of the signal. They are angle of insertion, penetration depth, and turbulence of the process flow (as at some flow rates there can be bubble formation). If a probe, which has a higher penetration depth than the sample height of the measurement in an experimental set up, is selected to use, the set up should be modified to increase the sample height than the required penetration depth. If the probe is going to be inserted to a small diameter pipe, where the penetration depth is higher than the diameter, and the probe cannot be inserted to the pipeline directly. In such a case, a flow cell with higher diameter should be included to the

existing line. The volume of the new flow cell should not be larger to create stagnant places, dead zones, and inhomogeneous mixture. This can be challenging because the plant needs to be shut down before the modification. The required mechanical interface may not be easy or straightforward at some instances. Therefore, the engineer experiences the dilemma whether he should select an analyzer, which fits to the system, or he should change the system to fit to the analyzer. Normally, process analytical instruments are superior in giving fast responses. If the interest is online monitoring of concentration changes or reaction kinetics, the analyzer should give fast responses such as measurements in every minute. Frequency of calibration/maintenance of the analyzer, cleaning requirement between successive scans, required training or expertise to operate the instrument, whether the instrument can be operated continuously throughout an entire process or an experiment cycle are also limiting factors.

Element 2: Process integration implies the method of measurement taken from the application. After selecting the required process analyzer, the sample measurement is carried out inline, at line or online. Examples for inline are: an immersion probe which directly contact with the sample inside the process equipment, process line or flow cell. In such an instance, sample dilution or probe cleaning prior to each measurement is impossible. On the other hand, the user has the ability to do so if there is an autonomous sampling system, which is called on-line. There are some process analyzers, which cannot be physically integrated to the process such as liquid chromatography. Samples that are withdrawn from the process (grab samples) either manually or automatically are measured offline and called at-line measurements. Grab samples associate with the highest percentage of sampling errors.

Element 3: Process analytical instruments give both qualitative and quantitative analysis. Qualitative analysis gives the first impression to understand whether it is meaningful and worth to develop a method for quantitative analysis by a particular instrument. Process analytical instruments are calibrated and validated before they are used to demonstrate that it is suitable for intended purpose. Normally, calibration means to ensure that the instrument readings are accurate with reference to established standards. Calibration can be used before using an instrument such as a weighing balance or a pH meter. Vendor specifies when and how frequently the equipment is needed to calibrate. Normally, the validation refers that the equipment installed correctly and performing without an error comparably to the one used before. These vendors' specified calibration and validation are straightforward.

However, in the PAT terminology, *calibration and validation* imply converting the instrument signals/measurements to be suitable to perform a specific analysis. Based on measurements taken as a set of samples (*calibration set*), a multivariate regression model is developed to predict an attribute. The model prediction performance is validated based on another set of samples (*validation set*) prepared under similar environmental conditions as the *calibration set*. The model is tuned until the prediction error becomes lower than an acceptable value. For example, a model can be developed based on measurements from a spectrometer performed for a calibration set and validation set to predict pH of some chemicals. The same instrument can be used to develop models for other applications such as determining a concentration of a sample, to determine individual concentrations in a mixture of chemicals or analyzing an impurity of a sample. These kinds of model developments to analyze indirect property



are the main expectation from a PAT tool. The method of model development is described under Section 3 for an application in a CO<sub>2</sub> capture process. The calibration and validation procedure should follow the guidelines specified in *Theory of Sampling (ToS)* [16] and *Design of Experiment (DoE)*.

Element 4: Data processing and chemometrics are a subcategory of model development stage. When it comes to the implementation stage of a process analyzer to the plant, the researcher has experience from laboratory experiments or batchwise experiments on what kind of data treatment is needed. Usually raw data coming out from a process analyzer such as a spectrometer contain noise. The information in the data is hidden within this noise. Preprocessing makes data easier to read, understand and interpret. There are also some instances where univariate methods are implemented and/or data processing is not essential. After preprocessing, the data can be used as input to a chemometric model such as a principle component analysis (PCA) model or partial least square regression (PLSR) model. Different chemometric tools have different advantages. For example, PCA can be used to identify trends of variation in the data with respect to time or process conditions, and PLSR can be used to predict process features based on indirect measurements. PLSR is widely used in process applications for quantitative purposes. One such example can be found in [17] where it shows the use of PLSR to quantify all chemical ions present in a CO<sub>2</sub> capture laboratory rig operated by aqueous amine. Another example of PLSR model development and ion speciation is shown in [18] for CO<sub>2</sub> capture by ammonia process. A detailed description for PLSR theory, calibration and validation is described in the literature [19, 20].

Element 5: Data acquisition and instrument control of a process analyzer is an essential part to integrate analyzer measurements with an automative control system. In the case of univariate analysis, implementation of automation control system is easy. However, when it comes to multivariate methods, communication between the process analytical instrument and the control system is challenging. There is a gap between these two types. The reasons are that the analyzer has different file formats and sometimes the control system has been implemented in a different file format in a different flat form. For example, in the analyzer, the data may be saved in csv file format and the control system implemented in MATLAB/LabVIEW interface needs data only from a wavelength range and needs data in txt or mat format as inputs.



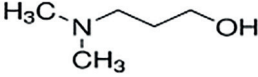
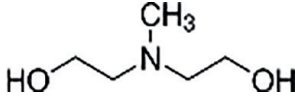
### **3. An experiment on developing a full calibration model using Raman spectroscopy**

The scope in this section is to present the methodology on how a process analytical instrument is implemented to replace traditional chemical analysis. The example described in this section is specific to CO<sub>2</sub> absorption process by amines, but a similar approach can be applied for any chemical analysis in laboratory or process plant. Analysis of CO<sub>2</sub> capture solvents is necessary almost in every R&D tasks and CO<sub>2</sub> process plants to optimize the absorption and desorption process. Some examples are investigating the effects of different types of solvents, blends, catalyzers, process parameters and equipment configuration on CO<sub>2</sub> absorption and desorption capacity.

In this example, it is shown how a Raman spectroscopy-based full spectrum calibration is performed using a laboratory experiment for four types of amines which are reacted with CO<sub>2</sub>. Sample types are described in **Table 1**. Two primary and two tertiary amines were used for preparing four regression models. The primary amines are 2-aminoethanol (MEA) and 3-amino-1-propanol (3-AP). Tertiary amines have a different chemical mechanism than primary and secondary amines when absorbing CO<sub>2</sub> and they can reach CO<sub>2</sub> loading capacity up to 1 mol CO<sub>2</sub>/mol amine. 3-dimethylamino-1-propanol (3DMA1P) and methyl diethanolamine (MDEA) are the two tertiary amines used in this experiment.

### 3.1. Sample preparation

For each model, a calibration and validation set was prepared to facilitate *test set validation* [21]. Number of samples in each calibration and validation set is given in **Table 1**. All the samples were prepared using analytical grade chemicals and Milli-Qwater (18.2 MΩ cm). Aqueous solutions and water were degassed using a rotavapor. First, two amine stock solutions having 30 w/w% (weight per total weight of solution) concentration were prepared and stirred in closed containers for 30 min using mechanical stirrers. Stirring helps to mix the two phases of water and solvent to get a homogeneous solution. CO<sub>2</sub> was bubbled into one stock solution until the whole amine sample was *maximum CO<sub>2</sub> loaded*. The meaning of *maximum CO<sub>2</sub> loaded* is that the solution is filled with equilibrium solubility of CO<sub>2</sub> at a given temperature and pressure. The time required to fully load the amine solution was calculated based on the data of volume of 30 w/w% amine sample, CO<sub>2</sub> bubbling flow rate, room temperature, pressure and equilibrium solubility. The CO<sub>2</sub> loaded amine solution was then stirred for 30 min in a closed vessel and left for 24 h at room temperature. The aim was to facilitate CO<sub>2</sub> gas dispersion homogeneously throughout the solution; to accelerate the reaction between gas and solvent and to reach equilibrated state. One gram from each stock solution was transferred to a beaker to titrate with 1 M hydrochloric acid (HCl) to determine amine

Name	Abbreviation	Chemical structure	Chemical category	Number of CO <sub>2</sub> loaded solutions	
				Calibration	Validation
2-Aminoethanol (monoethanolamine)	MEA		Primary amine	19	18
3-Amino-1-propanol	3-AP		Primary amine	22	20
3-dimethylamino-1-propanol	3DMA1P		Tertiary amine	21	20
Methyl diethanolamine	MDEA		Tertiary amine	21	20

**Table 1.** Description of samples in the calibration and validation set.

concentration. By mixing different ratios of CO<sub>2</sub> loaded amine solution with the other amine stock solution (CO<sub>2</sub> unloaded), a series of 38–42 different CO<sub>2</sub> loaded samples were prepared in 10 mL glass reactors. After the solution in each glass reactor reached equilibrium, a titration method (refer Section 3.2) was carried out to measure its true CO<sub>2</sub> concentration in units of moles CO<sub>2</sub> per mole solvent.

### 3.2. Analysis of reference samples

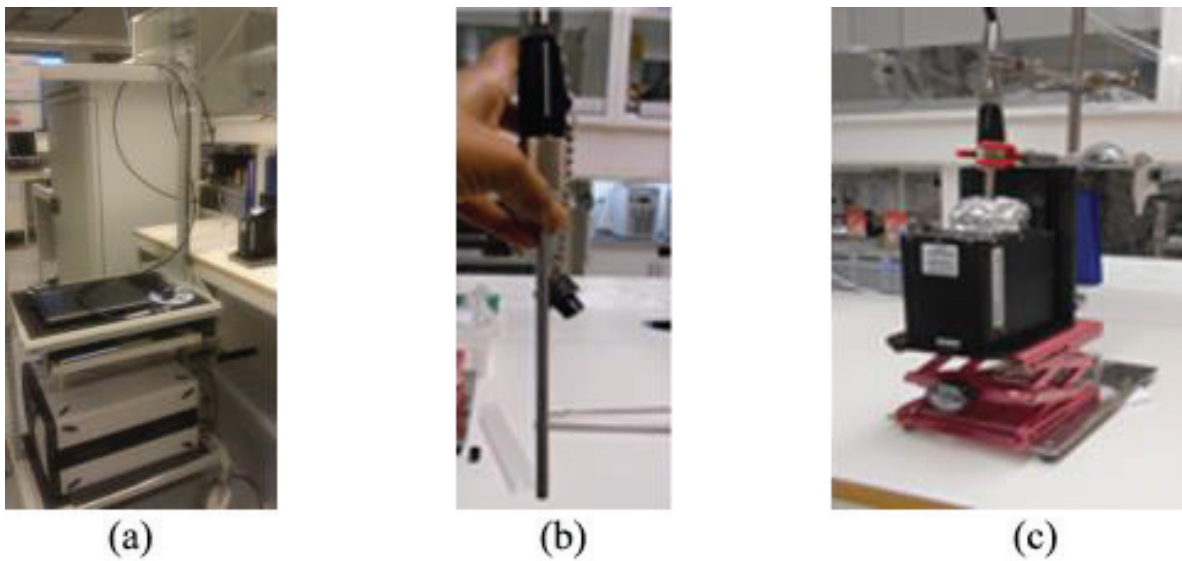
Determination of true CO<sub>2</sub> concentration (CO<sub>2</sub> loading) in alkanolamine samples was carried out by the *BaCl<sub>2</sub> titration-precipitation method*. 0.1 M Sodium hydroxide (NaOH), 0.1 M HCl, 1 M HCl, barium chloride (BaCl<sub>2</sub>) purchased from Merck (99%) and the titrator Mettler Toledo T50 were used for the experiment. The titration procedure is discussed in [22]. This titration is popular and a well-established method to analyze CO<sub>2</sub> loading in absorption processes both in laboratory and industrial applications. However, the method needs extensive chemical preparation; and it takes more than 2 h to analyze one sample and needs expertise and tedious manual work. The accuracy of the PLSR models is strongly affected by the accuracy and results of this analysis. All the sampling errors during sample extraction from stock solution, chemical preparation, weighing, transferring samples, dilution, filtering and titration were identified using a fish-bone analysis and addressed based on the knowledge from *Theory of Sampling* [16].

### 3.3. Raman spectroscopy

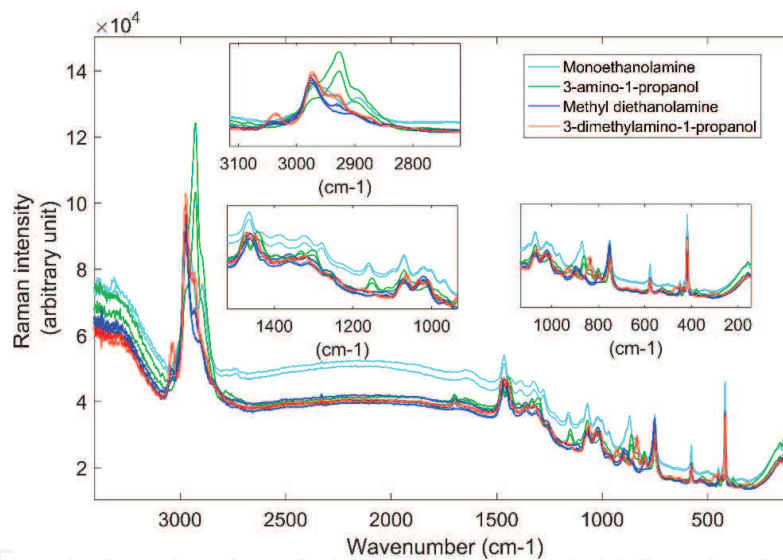
The Raman spectroscopy is a process analytical technique which can be used for batch-wise experiments where measurements are taken manually such as in laboratory tests, or for continuous operations such as in process plants where measurements can be taken continuously in each time interval. The instrument output is called a Raman spectrum which is a plot of intensity of scattered light (called Raman intensity) versus energy difference (given by wavenumber in cm<sup>-1</sup>). If the objective is to measure the concentration of a chemical sample using Raman spectroscopy, then the peaks and their intensity in a Raman spectrum indicate information about the type of chemicals and their composition respectively for the measured sample. Kaiser RXN2 Analyzer (as shown in **Figure 2a**) with 785 nm laser wavelength, 400 mW laser power and 100–3425 cm<sup>-1</sup> spectral range was the Raman spectrometer used in this experiment. An immersion optic probe was connected to the RXN2 Analyzer via a fiber optic cable (refer **Figure 2b**). During each measurement, the immersion probe was positioned vertically into the 10 mL glass reactor using a stand. The glass reactor was covered by a black box and aluminum foil to avoid interaction with fluorescence from external light sources (as shown in **Figure 2c**). Each scan was acquired as an average of six scans with 10 s over a total exposure time of 60 s to get a good signal-to-noise ratio.

### 3.4. Data processing

The aim of the data processing is to condition the measurement signal by removing as much as possible of unwanted structure from the data. Including noisy spectra in regression model



**Figure 2.** RXN2 analyzer; (a) Raman analyzer with exciting source and detector; (b) Raman immersion probe; (c) sample is in an enclosed sample compartment (black box) and probe, which is mounted vertically, takes measurements.



**Figure 3.** Unprocessed Raman spectrum for four types of CO<sub>2</sub> loaded amine solutions.

calibration results in poor correlation between property to be predicted and measured. The RXN2 analyzer was used to generate a data matrix of  $n \times p$  where  $n$  is number of objects (e.g., different samples or measurements with time) and  $p$  is 3326 of Raman wavenumbers. This data matrix contains the chemical fingerprints of the objects and typically different types of noise. This noise comes from interference of other chemical components, laser input variations, noise from fiber optic cable or inadequate path length for the laser.

**Figure 3** shows some raw spectra for four types of CO<sub>2</sub> loaded amines where normal features of Raman spectra are visible such as baseline shifts, scattering and peak overlaps. These features avoid the raw spectra to be used directly for the calibration model. Preprocessing of

raw spectra is recommended to improve the predictability of a regression model. There are several preprocessing methods available for PAT applications [23, 24]. The optimal choice of preprocessing method is specific to the application and instrument. In this analysis, the baseline correction based on the Whittaker filter [25] and mean centering was applied which provided the lowest prediction errors as presented by root mean square error of prediction.

### 3.4.1. Variable selection

When  $\text{CO}_2$  is reacted with an amine, it is converted into different carbon ions as shown in Eqs. (1)–(10). The variables related to all these carbon species should be included as *x variables* for PLSR modeling. However, with reference to **Figure 3**, isolation of these variables from the rest of the spectra is not straightforward. The spectroscopy shows measurements in the wavelength range from 100 to  $3425\text{ cm}^{-1}$ . In the model development, only a selected range of wavelength was included. The spectra for all the solvents (**Figure 3**) show noise which means unwanted variation, both in higher and lower frequency ranges. The middle frequency range shows a flat behavior with some offsets between measurements. The wavelength below  $400\text{ cm}^{-1}$ , between  $1600$  and  $2600\text{ cm}^{-1}$  and after  $3100\text{ cm}^{-1}$  was excluded to remove this noise possibly arising either from the instrument, cables or measurement probe. Since these measurements are associated with a chemical reaction, there are frequencies which are assigned to vibrational mode of molecules. The reaction between alkanolamine and carbon dioxide produces carbonate, bicarbonate and carbamate ions for primary and secondary amines. Reaction between  $\text{CO}_2$  and a tertiary amine does not form carbamate. For a  $\text{CO}_2$ -loaded amine solution, the vibrational modes from carbon species and amine species appear in the Raman spectra collectively which makes it more complex to study. One can understand what kind of chemical species present in a chemical system by observing peaks which vary with different concentrations. On the other hand, knowing what kind of chemical species present in the system helps to identify the peaks which should respond differently when concentration changes. This fact is very important when selecting variables for modeling. Having a small number of variables makes the model easier to interpret.

There are disadvantages having unwanted variables in the model. The biggest challenge is overfitting, which makes the model correlates with the property to be predicted (*y variable*) during the model development stage, but future samples predict poorly. For instance, when developing a PLS model to predict total  $\text{CO}_2$  loading in an aqueous MEA solution, important *x variables* are the vibrational modes coming from carbon species (i.e., carbonate, bicarbonate and carbamate ions). According to the vapor-liquid equilibrium in the system, the protonated MEA and free MEA concentrations correlate almost linearly with  $\text{CO}_2$  loading less than  $0.5\text{ mol CO}_2/\text{mol MEA}$  [9]. Therefore, by mistake, one can include the variables assigned to protonated MEA and free MEA to show a good correlation with  $\text{CO}_2$  concentration. However, when this model is used for samples except those are in the calibration and validation sets, predictions will be unreliable.

When there is little or no knowledge on how the *x variables* relate to the *y variable*, variable selection becomes further critical. In principle, all combinations of *x variables* must be tried to

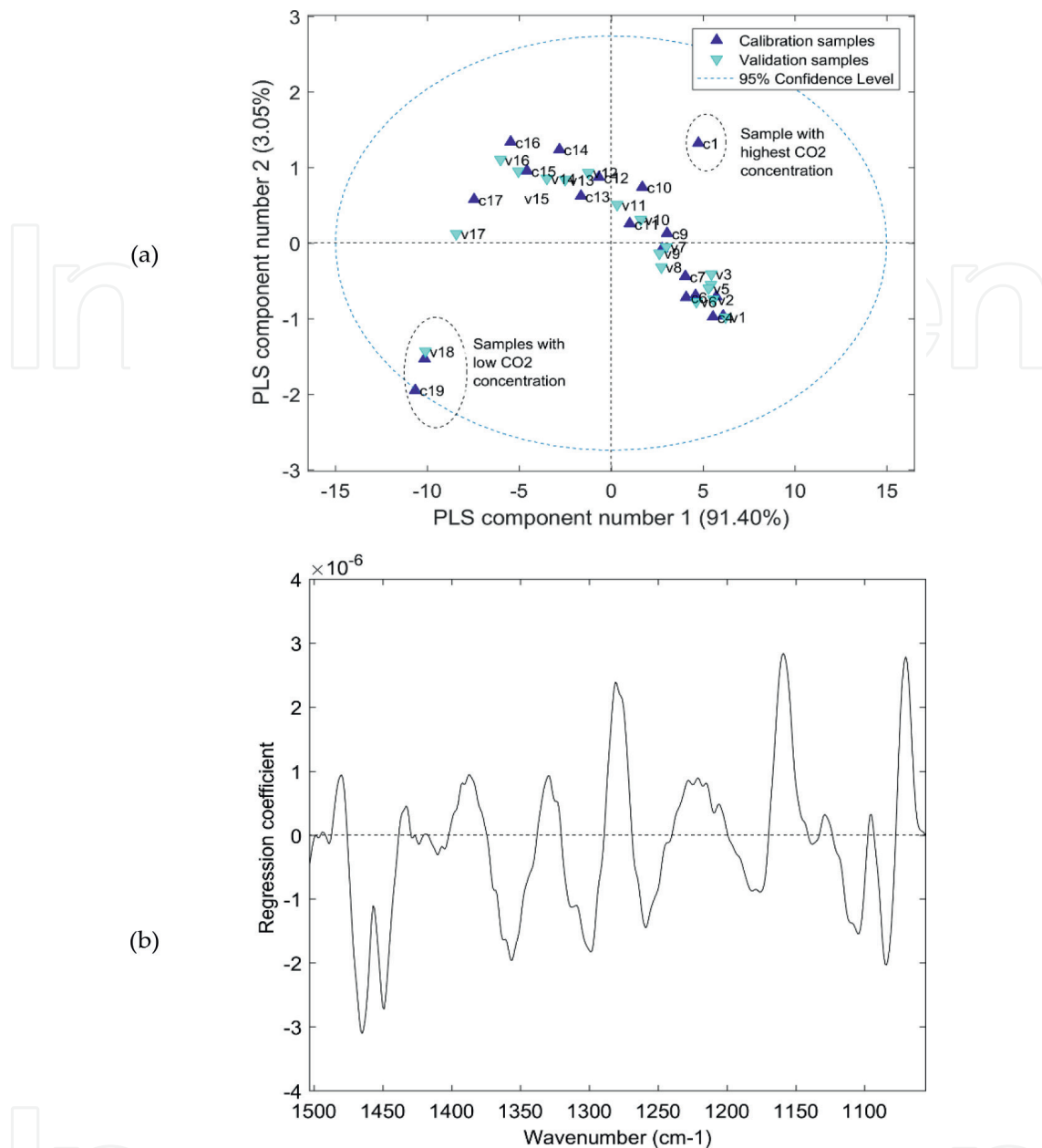
find the optimal choice which is not possible and practical. At such instances, variable selection methods such as iPLS (interval partial least squares regression), genetic algorithms (GA), selectivity ratio and jack-knife can be used [26]. Similar to finding the optimal preprocessing method, finding the optimal variable range is specific to the application and is an iterative procedure. In this example, the selection of the variable range for each model was performed which included vibrational modes of important carbon species available in literature [18]. Due to the overlapping of peaks, it was difficult to isolate the exact area for related vibrational modes and therefore 1000–1500 cm<sup>-1</sup> and 1000–1164 cm<sup>-1</sup> regions were selected for primary and tertiary amines respectively which made the models with the lowest RMSEPs.

### 3.5. Results

The calibration and validation results for each of the four respective PLSR models for CO<sub>2</sub> concentration in MEA, MDEA, 3-AP and 3-DMA1P solutions are presented in this section. Data preprocessing and model development were implemented in PLS Toolbox 8.21 in the MATLAB 2016a software (MathWorks Inc.).

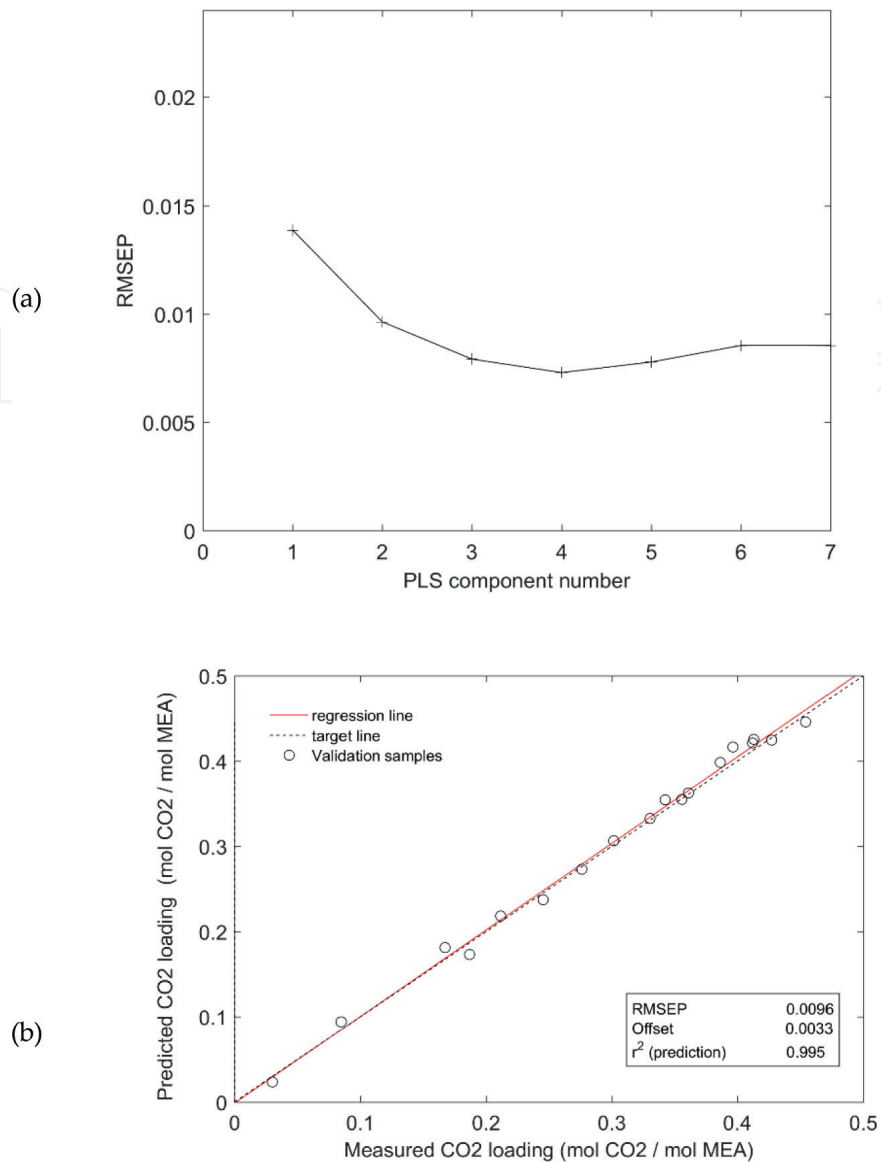
The model behavior is presented using four graphs for each amine solution (from **Figures 4–11**) which are the score plot ( $t_1$ – $t_2$ ), regression coefficients, RMSEP and predicted CO<sub>2</sub> loading versus the measured loading. In the plots,  $c$  represents calibration samples and  $v$  represents validation samples. Samples are numbered as 1, 2, 3, 4 onwards with decreasing CO<sub>2</sub> concentration. The regression coefficient plot is an indication on what weight of each wavenumber contributes to the prediction. The higher the regression weight, the higher the importance of the assigned wavelength to the prediction. The regression plot can be mapped with the vibrational modes of carbon species which are chemically important to the total CO<sub>2</sub> loading.

The score plot gives the overview of the span of the calibration data and validation data. Even without knowing the value of CO<sub>2</sub> loading ( $y$  variable), by visualizing the sample location in the score plot, one can understand whether the sample is highly or less concentrated with CO<sub>2</sub>. Score plot can also be used to identify outliers which mean samples that show nonrepresentative  $x$  variables. There can be various reasons for outliers such as impurities in samples, different sample type, instrument error and sampling errors. During the model development stage, if such outliers are identified, they should be carefully analyzed and removed from the model. When the model is used for process monitoring, visualization of such outliers helps in the quick identification of the abnormal behavior in the process. With the increasing number of PLS components, the prediction error of the models varies. A plot of RMSEP versus number of PLS components is used to conclude the required number of PLS components for the model. It is always preferable to select a small number of PLS components to avoid model complexities. An optimum number of PLS components avoids the risk of overfitting of the model. The aim of the model is to use the instrument for predicting CO<sub>2</sub> concentration. The predicted versus measured plots show how far the measured values deviate with respect to the predicted values for the validation set. This deviation is interpreted with statistical parameters such as  $r^2$ , RMSEP and offset. When *test set validation* is used, this plot gives an image on how the model will align with future data.



**Figure 4.** Results from PLSR model for MEA; (a) score plot of PLS components 1 vs. 2 showing calibration and validation samples; (b) regression coefficients based on a 2-component PLSR model.

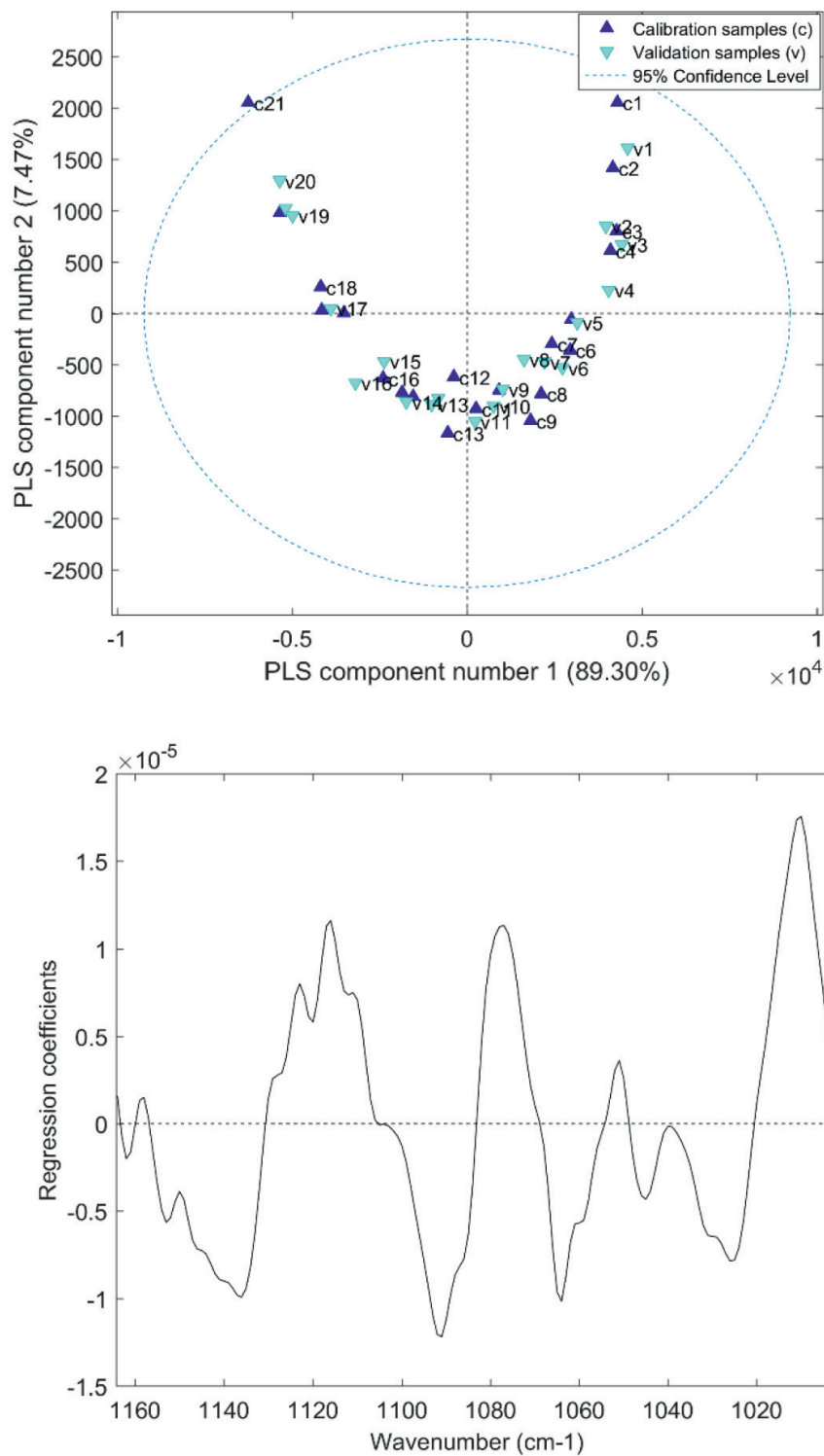
**Figure 4(a)** is the score plot of PLS component 1 vs. 2 for MEA model. According to this plot, PLS component 1 describes more than 90% of variation of data while PLS component 2 describes around 3% of variation. The sample with the highest CO<sub>2</sub> concentration (*c1*) and that with the lowest CO<sub>2</sub> concentration (*c19*, *v18*) appear isolated in the score plot implying they have extreme concentration values. The samples are spread in the plot as a pattern where they move from right to left in the direction of PLS component 1 as the concentration decreases. When this model is used for new data, they will appear in the same data swarm area. Samples with high CO<sub>2</sub> concentration will appear in the positive side of PLS component 1 and when



**Figure 5.** Results from PLSR model for MEA; (a) RMSEP with respect to number of PLS components and (b) predicted versus measured CO<sub>2</sub> loading.

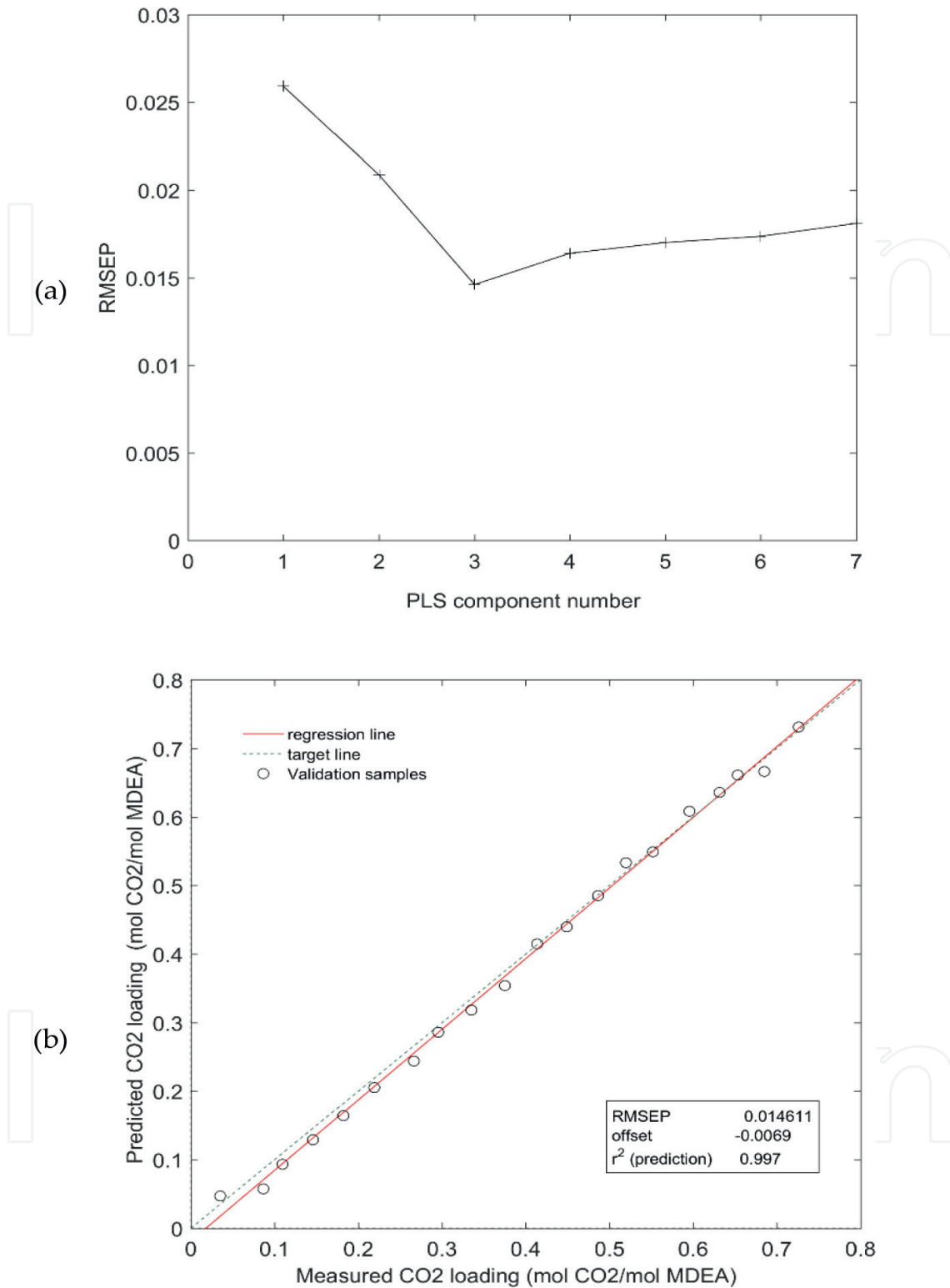
their concentration increases, they move toward the negative side of PLS component 1. **Figure 4(b)** is the plot of regression coefficients between the wavenumber 1000–1500 cm<sup>-1</sup>. Wavenumbers having positive and negative regression coefficients contribute positively and negatively respectively for the predicted property. **Figure 5(a)** shows the variation of RMSEP with increasing number of PLS component. According to this plot, RMSEP becomes the lowest at fourth PLS component. Having a higher number of PLS components in the model increases model complexity and include more noise to the model. There is not much difference in the prediction error between PLS component 2 and PLS component 4. Therefore, two PLS components were selected for the prediction model. **Figure 5(b)** shows how well the model fits when using for the validation data set to predict CO<sub>2</sub> concentration using their Raman spectra.





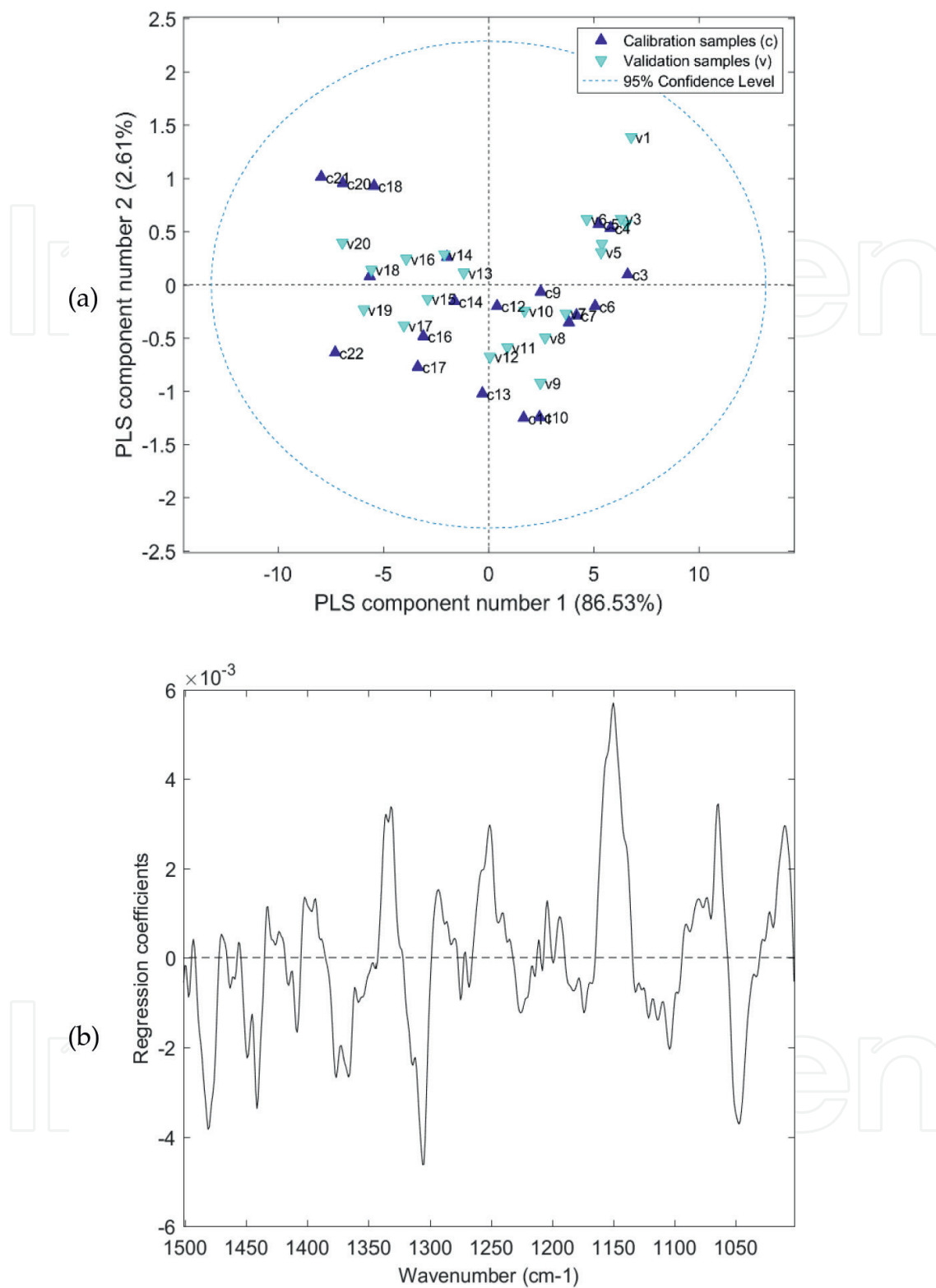
**Figure 6.** Results from PLSR model for MDEA; (a) score plot of PLS components 1 vs. 2 showing calibration and validation samples and (b) regression coefficients based on a 3-component PLSR model.

Similarly, in **Figure 6(a)**, score plot for the MDEA model shows a data swarm with a pattern moving from positive to negative side of PLS component 1 when the concentration decreases in MDEA samples. Plot of regression coefficients between wavenumber 1000 and 1164 cm<sup>-1</sup> as shown in **Figure 6(b)** indicates that there are both positively and negatively correlated



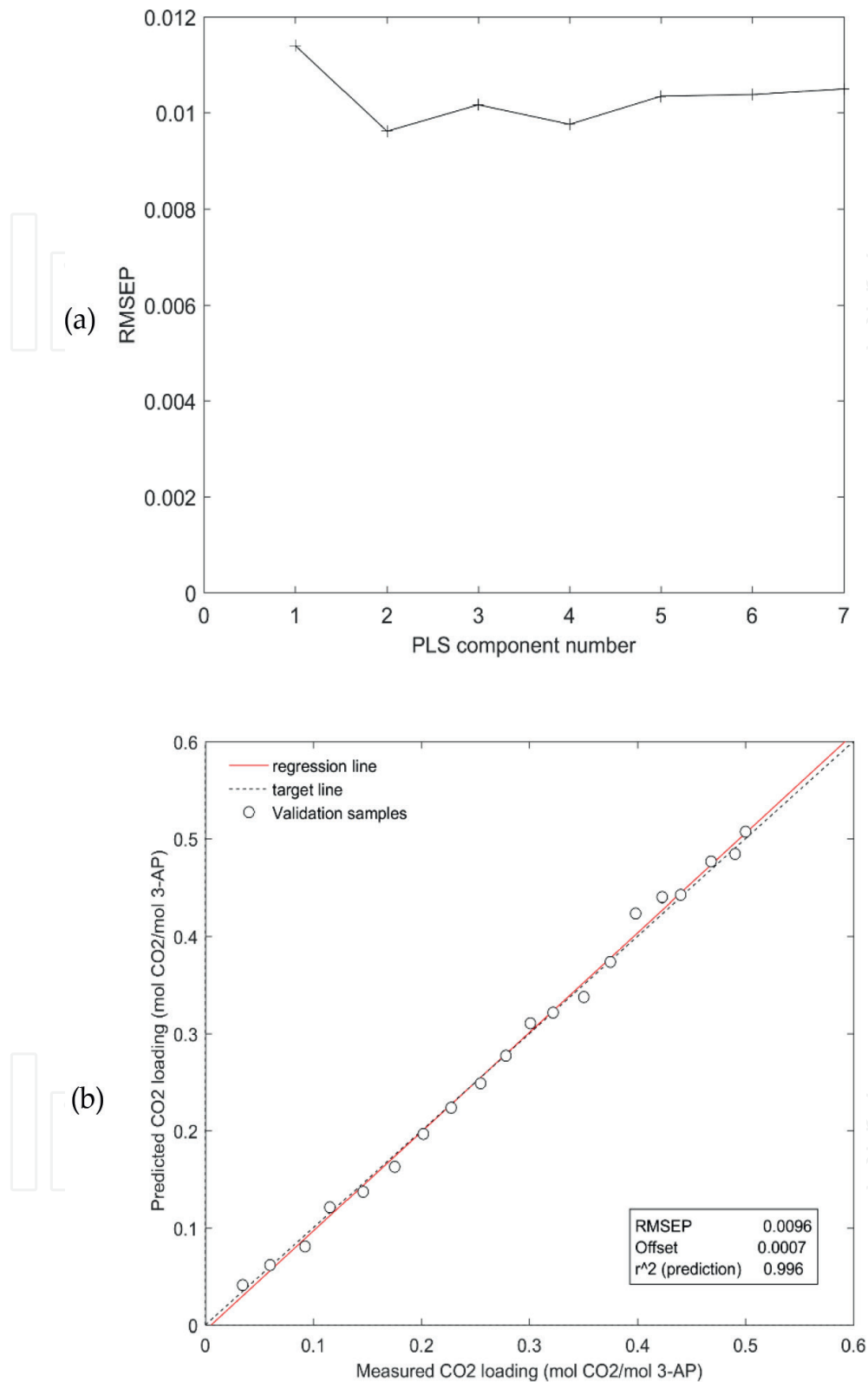
**Figure 7.** Results from PLSR model for MDEA; (a) RMSEP with respect to number of PLS components and (b) predicted versus measured CO<sub>2</sub> loading.

frequencies for the model in this range. Since the model shows the lowest RMSEP at PLS component 3 as given in **Figure 7(a)**, three components were selected for the model and model predictions for validation data set are shown in **Figure 7(b)** resulting an  $r^2$  of 0.995.



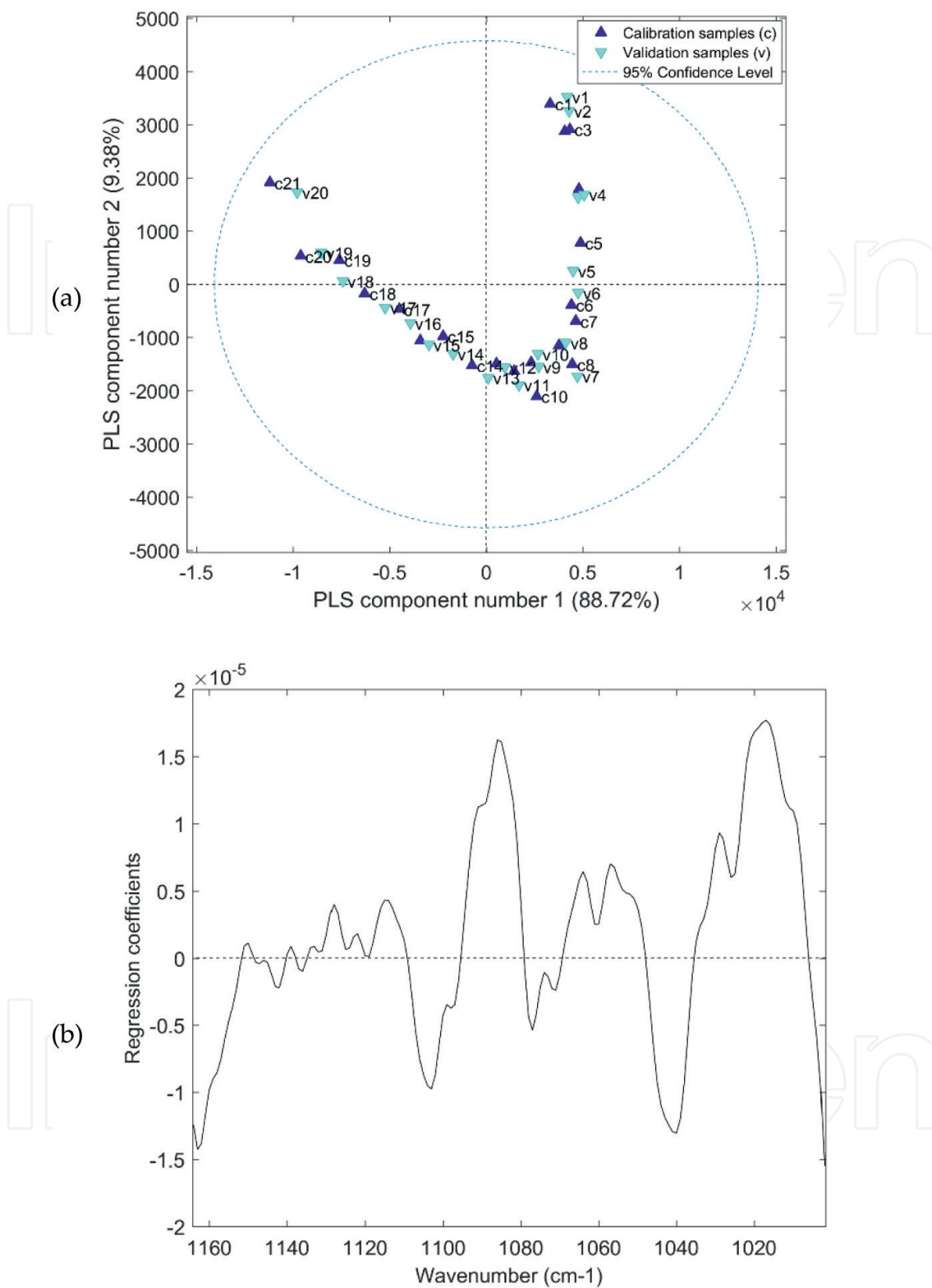
**Figure 8.** Results from PLSR model for 3-AP; (a) score plot of PLS components 1 vs. 2 showing calibration and validation samples and (b) regression coefficients based on a 2-component PLSR model.

**Figure 8(a)** shows the movement of samples from positive to negative side of PLS component 1 as the  $\text{CO}_2$  concentration decreases in  $\text{CO}_2$  loaded 3-AP solvent. The plot of regression coefficients between 1000 and 1500  $\text{cm}^{-1}$  as given in **Figure 8(b)** shows negatively and positively



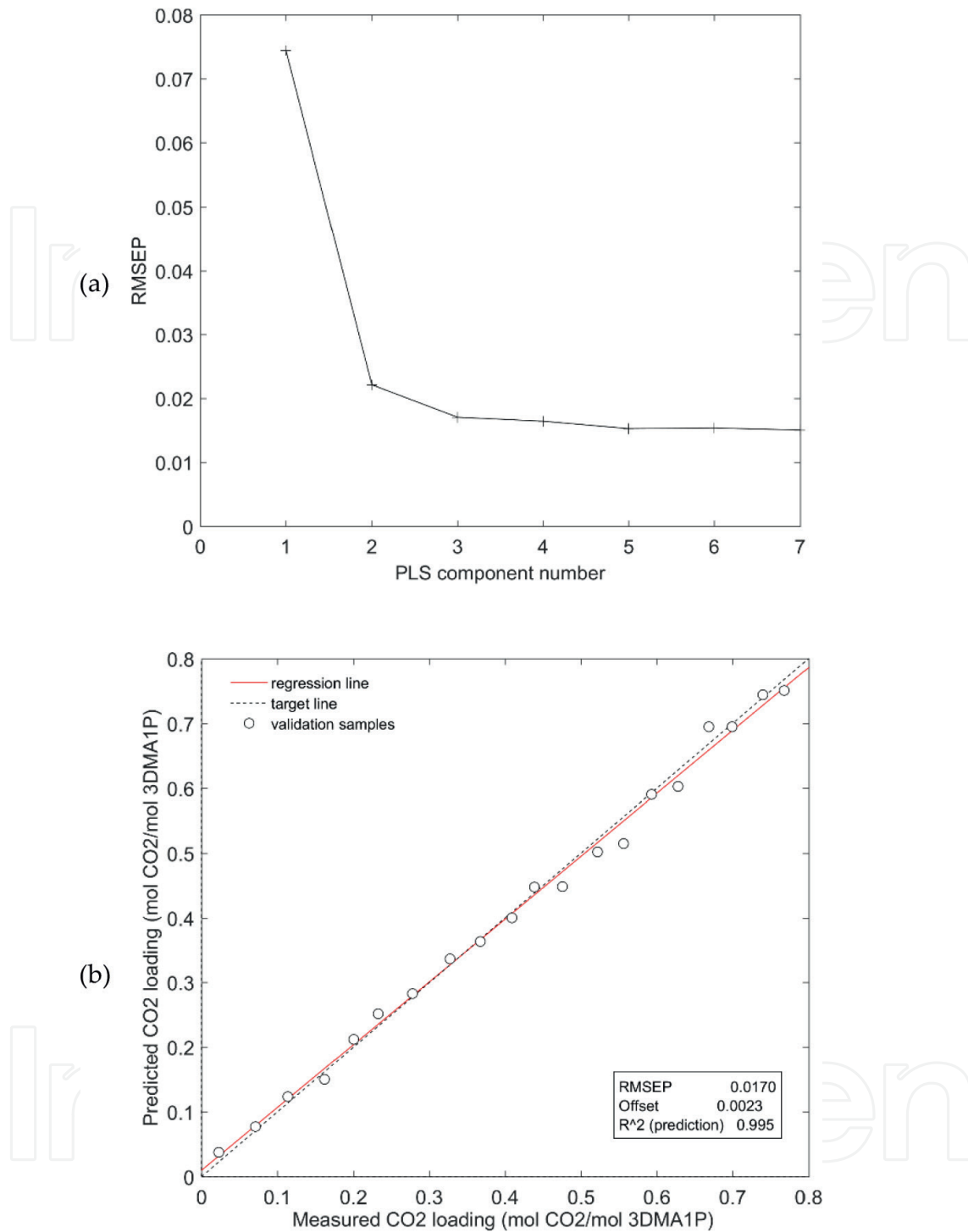
**Figure 9.** Results from PLSR model for 3-AP; (a) RMSEP with respect to number of PLS components and (b) predicted versus measured CO<sub>2</sub> loading.

correlated wavenumbers to the model predictions. According to RMSEP variation with respect to number of PLS components, two PLS components (**Figure 9(a)**) were selected for the model. **Figure 9(b)** shows how well model predicts for the test set samples. The model results



**Figure 10.** Results from PLSR model for 3DMA1P; (a) score plot of PLS components 1 vs. 2 showing calibration and validation samples and (b) regression coefficients based on a 3-component PLSR model.

for the tertiary amine 3DMA1P are shown in **Figures 10** and **11**. Similar to other solvents, the score plot shows a systematic variation of data swarm (**Figure 10(a)**) while **Figure 10(b)** shows the most and least important variables between 1000 and 1164  $\text{cm}^{-1}$  wavenumbers. Three PLS



**Figure 11.** Results from PLSR model for 3DMA1P; (a) RMSEP with respect to number of PLS components and (b) predicted versus measured CO<sub>2</sub> loading.

components were selected (**Figure 11(a)**) for solvent 3DMA1P, and the model predicts the validation samples with  $r^2$  of 0.995 (**Figure 11(b)**).

A summary of the model details for each amine solution is presented in **Table 2**. For all the predictions models, RMSEP percentages are less than 2.13% and  $r^2$  is  $\geq 0.995$ . Each PLSR model is valid only for the CO<sub>2</sub> loading range which is given in **Table 2**.

Model	CO <sub>2</sub> loading range (mol CO <sub>2</sub> /mol amine)	Variable range (cm <sup>-1</sup> )	PLS components	RMSEP (RMSEP %)	r <sup>2</sup>
MEA	0–0.4543	1000–1500	2	0.0096 (2.11)	0.995
3-AP	0–0.5149	1000–1500	2	0.0096 (1.86)	0.996
3DMA1P	0–0.7945	1000–1164	3	0.017 (2.13)	0.995
MDEA	0–0.7449	1000–1164	3	0.014 (1.88)	0.997

Table 2. Summary of PLSR models.

When these models are used for predictions of CO<sub>2</sub> loading in future samples, first their Raman spectra are preprocessed using Whittaker filter and mean centering. The required variable range is selected for each model and using the regression coefficient equation as shown in Eq. (11), the CO<sub>2</sub> loading is predicted.

$$Y = b_0 + b_1 X_1 + b_2 X_2 + b_3 X_3 + \dots + b_n X_n \quad (11)$$

In Eq. (11),  $Y$  is the predicted CO<sub>2</sub> concentration;  $b_0$  is regression coefficient for the intercept,  $X_n$  is the preprocessed  $n$ th variable (Raman wavenumber) and  $b_n$  is the regression coefficient relevant to variable  $X_n$ .

In PAT, chemometric modeling does not end once a model is calibrated and validated to achieve a targeted prediction accuracy and precision. The model is needed to undergo continuous improvement or remodeling. Some suggestions are assessing the current model performance using new validation data, using additional calibration data to remodel the existing model, improving data preprocessing methods, improving sampling methods, moving to more accurate reference analysis, different  $x$  variable ranges and including calibration samples with more variations.

## 4. Conclusions

Implementation of PAT tools in CO<sub>2</sub> capture process is useful in many ways to accelerate laboratory analysis, R&D tasks and full-scale plant operations. One such example is using a Raman spectroscopy to determine CO<sub>2</sub> concentration in alkanolamine solutions real-time. During the process of implementation of a process analyzer for such an application, a chemometrics-based calibration model should be prepared. Four PLSR models were developed to predict CO<sub>2</sub> concentration in two primary amines and two tertiary amines solutions during CO<sub>2</sub> absorption process. The models predictions are satisfactory where RMSEP are 2.11, 1.86, 2.13 and 1.88% for MEA, 3-AP, 3DMA1P and MDEA, respectively. The target of the present experimental work was to show the PLSR calibration model development for reaction between CO<sub>2</sub> aqueous amine solutions. Primary amine and tertiary amine type was selected for the study because they have two different types of reaction mechanisms. Hence, work on secondary alkanolamines, and so on was out of scope. However, we expect that creating

a model for secondary amines would be similar to the reported case of primary amine since both primary and secondary amines produce carbamate when reacted with CO<sub>2</sub>.

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## Conflict of interest

The authors in this paper declare no conflicts of interest.

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