

# System Development for On-line Monitoring using Raman Spectroscopy for CO<sub>2</sub> Absorption by MEA

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## Abstract

Among various kinds of technologies available, carbon dioxide (CO<sub>2</sub>) capture by monoethanolamine (MEA) is considered to be the most technically and scientifically matured technology which can be tested in industrial scale. When CO<sub>2</sub> is absorbed by an MEA, a chemical reaction takes place which results to form different carbon and amine species in the system. In this work, Raman spectroscopy has been used to measure those concentrations in-situ. Since the instrument does not provide direct measurements, multivariate analysis has been used to develop models and predictions are made using these models for future measurements. This study presents the methodology of acquiring measurements by the Raman spectroscopy for MEA-CO<sub>2</sub>-H<sub>2</sub>O system, transferring the measurement data into Matlab/Labview, converting data into concentration values and presenting the results in a graphical user interface. This software based platform makes the Raman spectroscopy to be accessed as a real-time instrument in CO<sub>2</sub> capture plants.

*Keywords:* CO<sub>2</sub> absorption by MEA, real-time monitoring, Raman spectroscopy, chemometrics, Labview

## 1 Introduction

68% of global anthropogenic greenhouse gas emissions comes from energy production and 90% of these greenhouse gases are carbon dioxide (IEA, 2017). Therefore capturing CO<sub>2</sub> emissions from energy production is a mandatory task under the climate change mitigation actions. As stated in (IEA, 2017) from 1870 to 2015, CO<sub>2</sub> emission by fossil fuels dramatically increased from near zero to over 33 Gt CO<sub>2</sub> which resulted fossil fuel power sector to be the largest source of greenhouse gas emissions. Greenhouse gases are responsible for increasing the world atmospheric temperature causing threatening impacts of climate change. While switching towards renewable and non-fossil fuel sources, the immediate action to reduce further CO<sub>2</sub> emission to the atmosphere is CO<sub>2</sub> capturing and storage from current emission sources.

After several studies on CO<sub>2</sub> capturing, the so-called ‘monoethanolamine technology’ or in other words, absorbing CO<sub>2</sub> chemically to an MEA solution is considered to be the most promising technology which

can be tested in industrial level. Some examples for MEA based commercial plants are Boundary Dam CO<sub>2</sub> capture plant and Cansolv CO<sub>2</sub> capture system in Canada. When a CO<sub>2</sub> molecule bounds to an MEA molecule, they are converted chemically into different reaction intermediates. Among them carbonate (CO<sub>3</sub><sup>2-</sup>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), carbamate (MEACOO<sup>-</sup>) and protonated MEA (MEA<sup>+</sup>) are prime important. There can also be free MEA and dissolved CO<sub>2</sub> (unreacted) in the system. In an overall perspective, if one wants to get an overview about the chemical concentration of an MEA-CO<sub>2</sub>-H<sub>2</sub>O system, concentrations of above-mentioned chemical intermediates should be presented. Knowing the concentrations of intermediates gives the benefit to understand reaction path, impact of process parameters to the CO<sub>2</sub> absorption, inputs to thermodynamic modelling and thus help to design and optimize the process.

Raman spectroscopy is a process analytical instrument. Fundamentally, it gives information on molecular vibrations and crystal structures in a chemical system. This information can be mapped with other properties of the system such as concentration of a chemical specie. Multivariate regression models can be developed to estimate those properties using the instrument. In the CO<sub>2</sub> capture field, the use of such types of instruments are gradually becoming popular due to their fast response, ability to locate in-situ and facility to integrate with process automatic control systems. The Applied Chemometrics and Research Group (ACRG) at University of South-Eastern Norway (USN) has developed a method using Raman spectroscopy to determine concentration profiles in an MEA-CO<sub>2</sub>-H<sub>2</sub>O system based on multivariate analysis (Jinadasa, Jens, Øi, & Halstensen, 2017). The developed method can be used for laboratory experiments, R&D tasks, pilot plant operations and commercial applications of the CO<sub>2</sub> absorption process. It features over the traditional offline analyses due to the fast response. We use two software packages to operate the Raman instrument. The iC Raman 4.1 software which comes together with Raman analyzer is used to configure instrument and acquire measurements while Matlab is used to convert these measurements to concentration values. So far, these steps are carried out manually. Although it takes a couple of minutes to take a measurement from the system, file transferring

between the two software packages and giving commands for data processing and calculations takes time. Therefore the current approach is time consuming.

This paper describes a system development that can join the two software packages into one platform and enables the Raman spectroscopy as a real time analyzer for measuring concentrations of chemical species of the MEA-CO<sub>2</sub>-H<sub>2</sub>O system. It is also compatible to use by plant operators who have no/less knowledge on working with the data processing and calculations by Matlab.

## 2 Problem Identification

Several offline analytical instruments and chemical methods are available such as titration, nuclear magnetic resonance (NMR) spectroscopy and chromatography to determine chemical concentration in MEA-CO<sub>2</sub>-H<sub>2</sub>O system. All these methods are time consuming. Titration by BaCl<sub>2</sub> is common and a well-established method but it needs massive chemical preparation and the analysis takes around 2 hours per sample. NMR spectroscopy and chromatography are mostly limited to laboratory because they do not fit well in plant operations. Spectroscopic methods need prior calibration according to application and are expensive. Some of the spectroscopic instruments cannot be located in an industrial environment.

A fast, online method to monitor CO<sub>2</sub> absorption is important in process control and optimization. Maintaining the chemical concentration of the process streams at required levels is important for getting the target output from the plant. After several feasibility studies, Raman spectroscopy was selected as one of preferable solutions to monitor concentrations in this process. Several studies have been performed using Raman spectroscopy to investigate the concentration profiles in CO<sub>2</sub> capture process by amines. The method developed by USN using Raman spectroscopy was tested and validated at a mini-pilot CO<sub>2</sub> capture plant in Porsgrunn (Jinadasa et al., 2017). In this method, multivariate regression models have been calibrated and validated using test set validation. The raw Raman signals from the instrument was pretreated using techniques available in chemometrics and the regression models are based on partial least squares regression (PLSR) which is a powerful multivariate modelling approach.

However, there is a weak point in this approach as we move between two software platforms to transfer data and calculate the concentration value for each measurement. This operation is carried out manually and prevent the analyzer from being an in-situ monitoring application eventhough the Raman analyzer can take measurements continuously within a few seconds.

## 2.1 Existing method vs proposed method

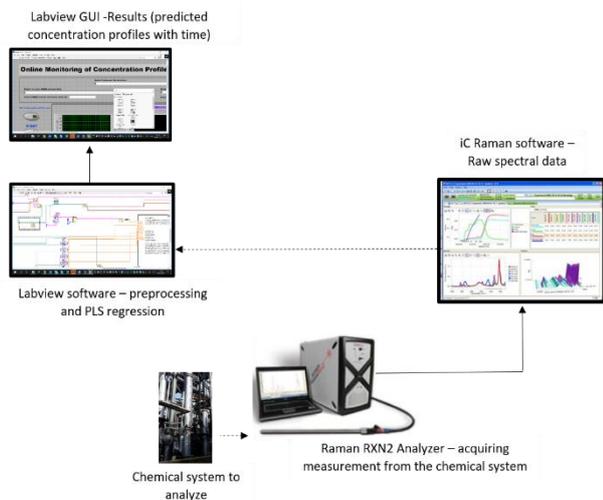
When the Raman instrument is used to measure the chemical information in MEA-CO<sub>2</sub>-H<sub>2</sub>O system, first the Raman probe is fixed into the system. A new file is open in iC Raman 4.1 software and suitable number of scans and laser exposure time is selected. (Kaiser, 2018) A file saving path and a file type (either .spc or .csv) for auto export is configured. When the command to measure the chemical system is given through the software, laser light is sent through the fibre optic cable to the Raman probe to go through the sample. After a scan is finished, a plot of Raman intensity vs Raman wavenumber is shown in the computer connected to the Raman instrument. The software simultaneously saves the data to a data file. To convert such a Raman measurement into a concentration value, the following steps are carried out:

- 1). Taking measurements from the process by running the iC Raman software – the measurements can be batch or continuous-wise
- 2). Saving the data in iC Raman software
- 3). Importing the data file into Matlab
- 4). Start PLS toolbox in Matlab (Eigenvector Research, 2018a)
- 5). Preprocessing the Raman data file using preprocessing methods in PLS toolbox
- 5). Input the data file to a PLS model which has been previously calibrated and validated
- 6). Run the PLS model to get the predicted concentration value
- 7). Showing the resulting concentration value

The disadvantage with this approach is that this system does not give the concentration value at the same time as the measurement is taken. It takes time to import the data from iC Raman software to Matlab and follow the preprocessing step. There should be always an operator to carry out the steps from 3 to 6. It requires knowledge and experience in operation of the mentioned software.

The proposed system aims at removing the barrier of manual file transferring and data processing steps between the two software to save time. In the proposed system there is no need of importing data from iC Raman software to Matlab interface. The user should first open the iC Raman software and Labview interface. After setting the data saving locations, number of scans per measurement and laser exposure time, both software can be started. The readings from the Raman instrument automatically transfers to the labview from iC Raman software. In the Matlab/Labview interface, this data is preprocessed and concentrations are predicted based on the PLS model automatically. Anyone who is not experienced with the software or analysis method can operate the instrument and read the required concentration profiles with time both as numerically and graphically. The predicted concentration data are also saved in an excel file. Figure 1 shows how the software

and hardware link together to get a concentration value using the Raman measurement and the proposed system.



**Figure 1.** Schematic of Raman spectroscopy measurement showing hardware and software links

### 3 System development

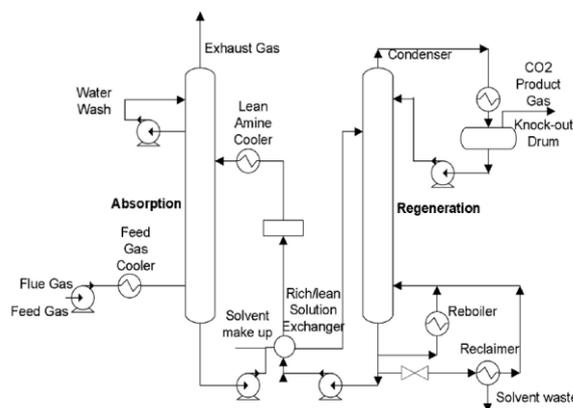
#### 3.1 Instrumentation

The Raman spectrometer available at USN is the Kaiser RXN2 Analyzer with 785 nm laser wavelength, 400 mW maximum laser power and 100-3425  $\text{cm}^{-1}$  spectral range. An immersion optic probe is connected to the RXN2 Analyzer via a fibre optic cable. When the analyzer is switched on to take a measurement, the laser light reaches the molecules in the sample, scattered and the Raman scattered light is filtered by the analyzer. The output display is a plot of Raman intensity (y-axis) which is the Raman scattered radiation and Raman wavenumber (x-axis) which is the frequency difference from the incident radiation (Kaiser, 2018). Peaks and their intensity which appear in this plot carry information about the chemicals present in the system and their composition respectively.

#### 3.2 Process description

The process of  $\text{CO}_2$  capture by amine using an absorption column is shown in Figure 2. Flue gas which contains  $\text{CO}_2$  is fed upward to the absorber. The  $\text{CO}_2$  free flue gas goes out from the top plate of the absorber. The absorbing agent, which is an amine solvent is fed to the top plate of the absorber. This stream is called the 'lean amine' stream. While it flows through the absorber it absorbs  $\text{CO}_2$  in the flue gas. The  $\text{CO}_2$  rich amine flows out from the absorber bottom plate and this stream is called the 'rich amine' stream. In industry, the difference between  $\text{CO}_2$  concentrations in the lean and rich streams is used as an important indicator to know

how much  $\text{CO}_2$  is absorbed by the amine. The concentration of other species are also important to yield the maximum process efficiency. The Raman RXN2 analyzer comes with four channels with facility to connect four Raman immersion probes to one analyzer thus providing to measure four streams simultaneously. The aim of this study was to optimize the absorption process in a  $\text{CO}_2$  capture process and hence configuration was set for two Raman probes to take measurements from both lean and rich streams.



**Figure 2.** Process flow diagram of  $\text{CO}_2$  capture absorption by amine (T. Li & Keener, 2016)

#### 3.3 Data treatment

The outcome of a measurement series using RXN2 Analyzer is a data matrix of  $n \times p$  where  $n$  is number of objects (eg: it can be different samples or signals with time) and  $p$  is 3326 Raman wavenumbers. Since this data matrix contains noise, preprocessing is needed before a model can be calibrated based on the PLSR algorithm. By performing such a data treatment, the noise generated due to interference of other chemical components, laser input variations or instrument noise can be minimized and the model predictability can be improved. There are different preprocessing techniques available in multivariate data analysis. The choice of which pre-processing method depends on many factors such as the instrument type, sample, impurities in the sample, environmental factors and properties of interest to measure. Based on our previous experience in developing PLS models for Raman measurements in MEA- $\text{CO}_2$ - $\text{H}_2\text{O}$  systems, three combinations of multivariate data processing methods showed lowest prediction error. They were scripted as Matlab codes which were the baseline-whittaker filter, standard normal variate (SNV) and mean centering.

### 3.4 Estimation of concentrations using the Partial Least Square Regression (PLSR) algorithm

There are different algorithms to develop a PLS model (Andersson, 2009). PLS is available in many commercial software packages, such as The Unscrambler, PLS Toolbox, ProSensus and SIMCA-P. To be independent from using commercial software packages except Matlab/Labview, Matlab codes were used in this study. PLS calibration and validation using the so-called 'test set' method and data pretreatment were coded in Matlab. Procedures mentioned in `pls.m`, `pretreat.m` available at libPLS package was used for PLS regression and mean centering (H.-D. Li, Xu, & Liang, 2018). `snv.m` file and `wlsbaseline.m` file available at PLS toolbox were referred for SNV and whittaker filter coding (Eigenvector Research, 2018b). The values for regression coefficients for each specie was stored in an `m`-file called `regcon.m` file and after data pretreatment, prediction was performed using the equation of regression coefficient values.

Figure 3 shows the flow path when the proposed system is in operation. After launching the iC Raman software the user selects a location to save Raman files in csv format for rich and lean stream. Each measurement is saved according to the format of "name\_date\_time\_sample name" and hence each file is uniquely distinguished. Then the user should move to the Labview GUI and enter the input variables. These variables are the locations of Labview file, location where Raman measurements from lean and rich stream are saved by iC Raman software and location where the predicted concentrations from matlab/labview system for lean and rich stream should be saved as excel files. After entering these inputs, both iC Raman software and labview are started. As shown in Figure 3, after setting the Raman data saving folder path (for lean and rich stream) and locating a location to save predicted concentrations (excel files), the Labview file start searching for a new Raman measurement file. When such a file is found, it is fed as an input to the PLS model. This is the only input variable to the PLS model. Output variable from the PLS model is concentration of specie. For each specie, there is a specific PLS model. Each PLS model gives the output value at the same time.

## 4 Results and Discussion

### 4.1 LabVIEW-based software platform

According to Figure 4, the GUI of the Labview based system shows the total CO<sub>2</sub> concentration and five concentrations of chemical species present in both lean and rich amine streams in a CO<sub>2</sub> capture process. The first graph in Figure 4 shows CO<sub>2</sub> concentration in units

of mol per mol MEA. The second graph shows concentration of free (unreacted MEA) and protonated MEA in units of mol per kg of H<sub>2</sub>O. The third graph shows concentration of carbonate, bicarbonate and carbamate in units of mols per kg H<sub>2</sub>O.

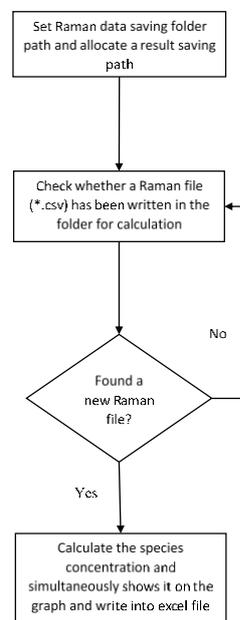


Figure 3. System flow sheet

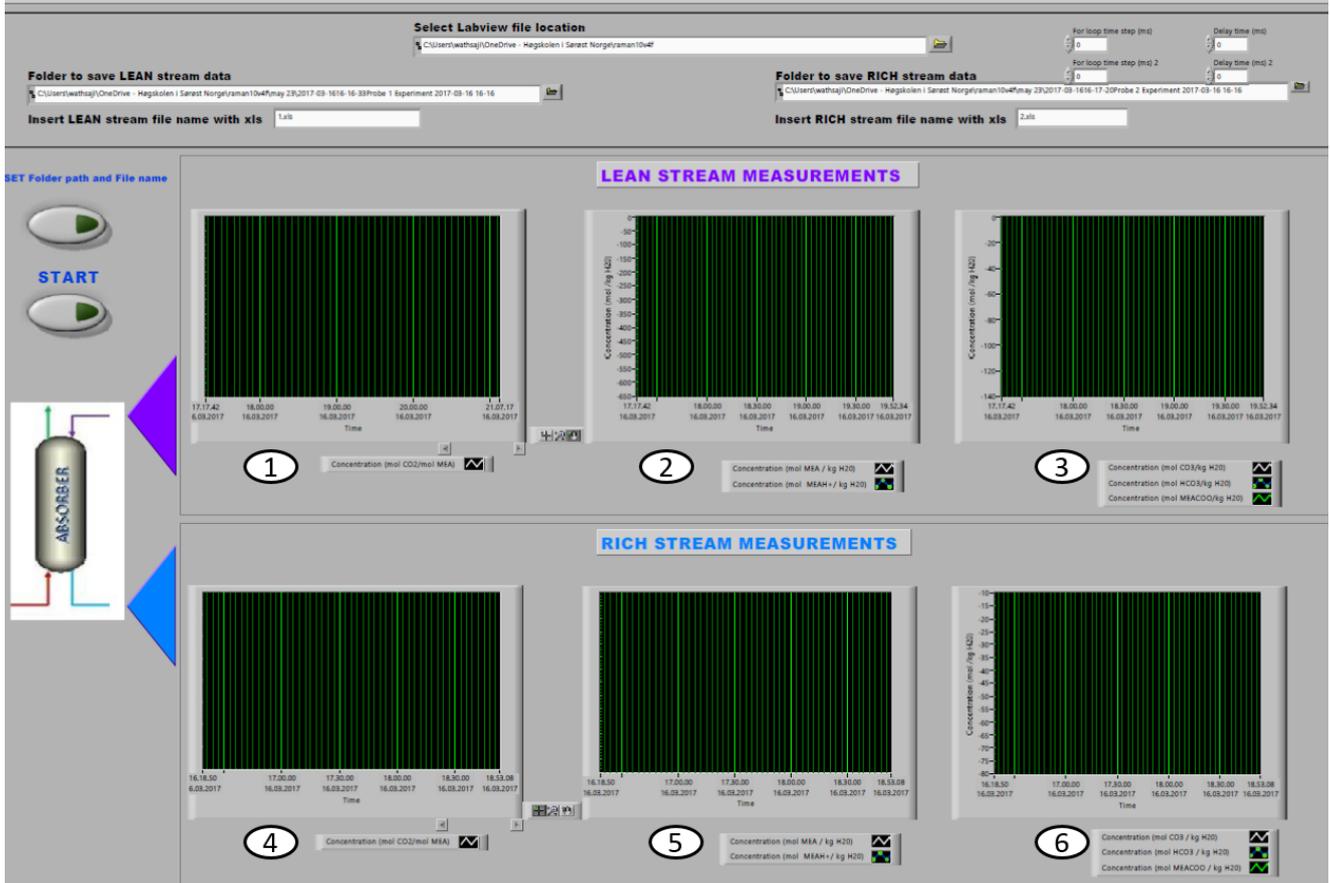
To show how the online predicted concentration of CO<sub>2</sub> loading matches with offline titration Table 1 provides results of a CO<sub>2</sub> loaded process stream with decreasing CO<sub>2</sub> concentration and prediction error. During this experiment, the Raman spectroscopy was connected to the process stream

Table 1. Validation of the online monitoring system with offline measurements

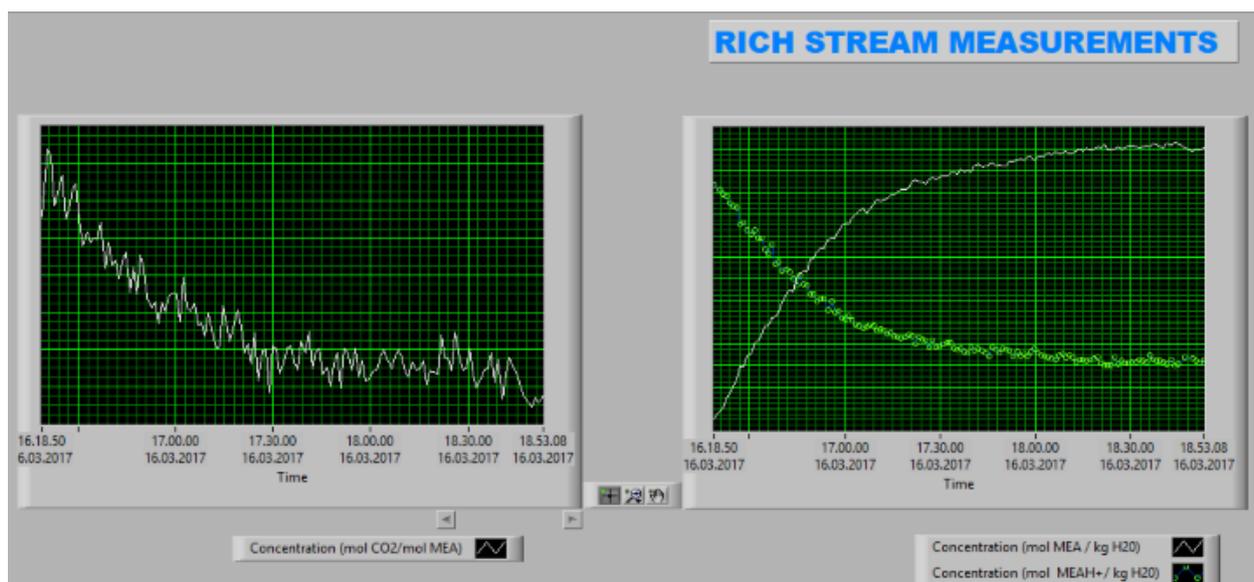
Time	CO <sub>2</sub> loading (mol CO <sub>2</sub> / mols MEA)	
	Raman spectroscopy-predictions from online system ± prediction error	Offline titration results
15:15:56	0.491672 ± 0.0150	0.484216
15:35:41	0.481887 ± 0.0150	0.463091
15:55:26	0.489647 ± 0.0148	0.462196
16:16:21	0.44994 ± 0.0145	0.42835
16.35.08	0.350732 ± 0.0146	0.331385
16.56.04	0.262569 ± 0.0144	0.28351
17.15.53	0.196636 ± 0.0150	0.191744

The concentrations recorded by the Raman system closely match with the offline measurements for CO<sub>2</sub> loading. The average prediction error for Raman measurement is 0.015 mol CO<sub>2</sub> / mol MEA.

# Online Monitoring of Concentration Profiles in CO<sub>2</sub>-MEA-H<sub>2</sub>O System



**Figure 4.** Graphical user interface for concentration profiles; plot 1, plot 2 and plot 3 are CO<sub>2</sub> loading, MEA/MEA<sup>+</sup> concentrations and CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup>/MEACOO<sup>-</sup> for lean stream ; plot 4, plot 5 and plot 6 are CO<sub>2</sub> loading, MEA/MEA<sup>+</sup> concentrations and CO<sub>3</sub><sup>2-</sup>/HCO<sub>3</sub><sup>-</sup>/MEACOO<sup>-</sup> for rich stream



**Figure 5.** Example for recording real-time measurement for CO<sub>2</sub> loading and MEA/MEA<sup>+</sup> concentration in rich stream for two and half hour continuous operation of CO<sub>2</sub> desorption process

## 5 Conclusion and future work

Determining CO<sub>2</sub> absorption in liquid phase of MEA-CO<sub>2</sub>-H<sub>2</sub>O system by an analytical technique is useful in many aspects. It saves time and gives access to online monitoring of the system. The accuracy of laboratory methods is based on the skill of the analyst, demand time, labour and resource. Offline laboratory methods cannot be used for process automation. Eventhough, these traditional methods are still used to control the process parameters in CO<sub>2</sub> plants due to the non-availability of in-situ analysis methods.

In this paper, we present the development of Labview/Matlab based software platform which is connected to iC Raman software in Raman RXN2 Analyzer. The platform provides concentration profiles of different chemical species present in an MEA-CO<sub>2</sub>-H<sub>2</sub>O system. These concentration values are calculated indirectly from measurements from Raman analyzer. The calculation is based on partial least square regression method. PLS and data pretreatment algorithms were written as matlab scripts.

If a calibration and validation data set is available, this system can be easily modified to another amine based CO<sub>2</sub> capture system without extensive effort. For instance, there are other amines which have the ability to absorb CO<sub>2</sub> and Raman instrument can be used to determine the total CO<sub>2</sub> absorbed and the concentration of other chemical species. If the user needs to use this GUI for such amines, he can input new calibration and validation data set into PLS script and change the preprocessing script in Matlab accordingly. The developed system can also be used to monitor how the reaction between an amine and CO<sub>2</sub> evolves with time in a batch reaction.

It is also recommended to take the use of the data to perform other chemometric analysis such as principle component analysis, outlier detection and multivariate curve resolution to better understand the chemical system. The plots related to these analysis can be implemented in the developed GUI similar to the concentration plots.

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