

Multi-component analysis of monoethanolamine solvent samples by FTIR

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ABSTRACT

Partial least square regression (PLS-R) methodology have been applied on dataset containing FTIR spectra and densities for a large set of MEA solvent samples. The prediction capabilities for the major compounds were tested on different set of realistic degraded solvent samples ranging from bench scale experiments to pilot plant campaigns. Generally, the methods showed good results with exception of samples with high amount of heat stable salts (HSS). For the real samples, sample residuals (i.e. part of data not fitted by the model) were also studied, and a clear correlation between the residuals and HSS level in samples were observed. Online techniques based on PLS-R and FTIR should be an attractive alternative for monitoring the major solvent compounds in CO₂ capture plants using amine solvents, as this will reduce cost of chemical analysis and could be an important tool for implementation of control strategies for energy saving in the process.

1. Introduction

CO₂ capture processes must be operated optimally in order to ensure minimization of CO₂ removal cost, emissions to air and solvent longevity. Efficient operation requires optimization of process conditions, set points and allowable tolerances for a given capture scenario. In the case of post-combustion carbon capture where power generation is the primary function of the operating plant, the CO₂ capture system must respond quickly to varying plant loads in order to ensure that CO₂ emissions are maintained below a given threshold. Reliably operating a CO₂ capture process at or near optimal conditions in response to fluctuating plant loads becomes a dynamic and potentially complex problem requiring advanced on-line telemetry and well-developed process control strategies. Dynamic operation is seen as a likely scenario for a future solvent based CO₂ capture plants, and online telemetry, capable of monitoring gas and liquid compositions throughout the capture process, becomes a vital tool for implementation of control strategies for energy saving in the process.

Many of today's promising CO₂ capture solvents incorporate blends of amines and / or other additives, which need to be monitored and maintained for optimal performance. Commercially available industrial instrumentation for online compositional analysis is generally limited to that of gas phase streams in CO₂ capture processes. Determination of solvent concentrations (amines, water, CO₂, etc.) is typically conducted off-line, requiring manual sampling and laboratory analysis. The Off-line analytics do not provide immediate feedback to the current state of the process and the analysis may also be expensive. CO₂-loading, blend

composition and water content are dynamic solvent parameters directly related to the process performance. In long-term processes solvent degradation and accumulation of unwanted contaminants may cause severe problems and methodology which could alert when build up or changes occur in the solvent may give valuable improvement in operating systems. Online techniques should be an attractive alternative for monitoring of solvents if they can provide the major compounds of the solvent (amine, CO₂, water), are robust and easy to use as well as having low cost.

Infrared spectroscopy is a technique that is been used in food and other industry for chemical quality and process control, and Fourier transform infrared spectroscopy (FTIR) is regarded as an appealing technology because simple, rapid and nondestructive measurements of chemical components can be obtained (Rodriguez-Saona and Allendorf, 2011). FTIR spectrometry has the advantage that several components can be determined simultaneously, and the monitoring can be performed continuously (Einbu et al., 2012). Vibrational spectroscopy like FTIR is well suited to be used with multivariate calibration, as each observation is characterized by analytical signal/absorbance recorded at multiple wavelengths (Tomuta et al., 2018). Among multivariate data analysis, Partial Least Squares regression (PLS-R) are often used for treatment of such data (Rathore et al., 2011). PLS-R is a generalization of multiple linear regression (MLR) and can analyze data with strongly correlated, noisy and numerous X-variables and simultaneously model several response variables (Wold et al., 2001).

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Nomenclature

ATR	Attenuated Total Reflection
DEA	Diethanolamine
FTIR	Fourier Transform Infrared Spectroscopy
HeGly	N-(2-hydroxyethyl)-glycine
HEPO	4-(2-hydroxyethyl)-2-piperazinone
HSS	Heat Stable Salts
IC	Ion Chromatography
LC-MS	Liquid chromatography combined with Mass Spectrometry
MEA	Monoethanolamine

MEA Urea	N,N'-bis(2-hydroxyethyl)-urea
MLR	Multiple linear regression
NIPALS	Nonlinear Iterative Partial Least Squares
PLS-R	Partial Least Square regression
RMSEC	Root Mean Square Error of Calibration
RMSEP	Root Mean Square Error of Prediction
RMSEV	Root Mean Square Error of Validation
SDR	Solvent Degradation Rig
SQRT	Square Root
TCM	Technology Center Mongstad
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon

conjunction with Attenuated Total Reflectance (ATR) has previously been demonstrated for measurements of concentration of 2-ethanolamine (MEA) and CO₂-loading (mol CO₂/mol amine) in a process stream, by the use of a Partial Least Squares regression (PLS-R) calibration model (Einbu et al., 2012). There are also several other studies where FTIR have been applied for determination of composition in amine solvents (Richner and Puxty, 2012; Kachko et al., 2016; Robinson et al., 2012; Motang, 2015; Diab et al., 2012; Gifftja, 2013). Some of the studies are for online specification in VLE measurements and lab reactors and some are related to demonstration of models for synthetic samples. Studies in larger scale such as pilot plants are more limited and also studies with aging solvents are very limited.

This work is focused on the PLS-R models and further improvement of robustness as well as attempt of extended calibration functionalities. The MEA calibration set used by Einbu et al. (2012) is also used in this study. In addition, spectral analysis of realistically degraded solvent samples ranging from bench scale experiments to pilot plants as well as spiked MEA samples with a range of degradation products is produced and applied for validation.

2. Experimental and methods

2.1. Experimental

The results of the current work are based on calibration models developed from a large set of solvent samples of known concentration and corresponding FTIR spectra. The preparation of the main calibration set as well as the corresponding spectra is described by Einbu et al. (2012). In this study this data set were extended with the corresponding densities and also water concentrations.

The MEA samples spiked with degradation products were prepared gravimetrically. For the real/aged samples, analysis of MEA, CO₂ and water were mainly done by LC-MS, TIC/TOC analyzer (operated in TIC mode) and Karl Fischer titration respectively. These results were used as reference concentrations in the study. All corresponding spectra with 32 cm⁻¹ resolution were obtained on ABB MB3000 Serie Laboratory FTIR spectrometer using a Pike MIRacle™ ATR cell with diamond as crystal. The measured spectral range was 700-4000 cm⁻¹. In addition, density was determined at 22 °C using a Mettler-Toledo CM40 Density Meter.

2.2. Spectral pre-treatment

As the spectra for real/aged samples were recorded at different times and some years later than the calibration set a correction was done to the spectra's recorded later than the calibration set. This correction was based on standardization of the spectra with respect to 30% MEA (unloaded), and the correction were done according to the following equation:

$$I_{\text{Corr.}}(\lambda) = I \cdot \alpha \cdot (\beta + \gamma \cdot \lambda) \quad (1)$$

With each set of samples recorded a sample of 30% MEA were included. The coefficients in Eq. (1) were determined by an iterative calculation scheme where the newly recorded spectra of 30 wt.% MEA and the 30% spectra from the calibration set were used. The scheme was as follows:

- At start $\beta = 1$ and $\gamma = 0$.
- α was determined by minimizing the sum of squares of deviation (SSD) between I_{Corr} and $I_{\text{Cal set}}$. This minimizing was done using the SOLVER function in MS-Excel™.
- β and γ were then determined by linear regressing of the difference $I_{\text{Corr}} - I_{\text{Cal set}}$ against λ .
- Step b) and c) was then repeated until no significant reduction in SSD.

The correction was checked with applying the correction to newly recorded samples of 10% MEA and 20% MEA and compare them with their respective spectra from the calibration set.

When working with spectra, some pre-treatment (transformation) prior to the PLS-R may lead to better results. One commonly used transformation is the use of derivative spectra's (first or second derivatives) (Esbensen et al., 2009). In this work a first and second derivatives by using Savitzky-Golay differentiation as well as a square root transformation (SQRT) was applied to the spectra of the calibration set. For the Savitzky-Golay differentiation a 4th order polynomial was used. The use of 2nd derivative Savitzky-Golay did not yield improvement compared to untreated spectra, while the 1st derivative Savitzky-Golay yield improvement for CO₂. The square root transformation yielded reduction in root mean square error (RMSE) for all components. A comparison of estimated RMSE using transformed and untransformed spectra are shown in Table 1. The calculations were performed on identical dataset (i.e. with same samples and same spectral region).

The RMSE is calculated according to the following equation:

$$RMSE = \sqrt{\frac{\sum (C_{\text{calc}} - C_{\text{Ref}})^2}{n}} \quad (2)$$

where C_{calc} – model predicted concentration, C_{Ref} – reference solution

Table 1

Root mean square error of calibration (RMSEC) and validation (RMSEV) with and without transformation (used factors are 4 in all cases). Cross validation with random segments of 10 applied for calculation of RMSEV.

	RMSEC [mol/kg]			RMSEV [mol/kg]		
	MEA	H ₂ O	CO ₂	MEA	H ₂ O	CO ₂
No transformation	0.1346	0.5417	0.0712	0.1523	0.6150	0.0784
1 st derivative Savitzky-Golay	0.1342	0.5466	0.0498	0.1496	0.6013	0.0515
2 nd derivative Savitzky-Golay	0.1892	0.6167	0.0859	0.2161	0.7350	0.0976
SQRT transformation	0.0843	0.3265	0.0282	0.0958	0.3603	0.0300

Table 2

Root mean square error of calibration (RMSEC) and validation (RMSEV) of the 4 PLS models (4 factors are used in all cases). Cross validation with random segments of 10.

	RMSEC [mol/kg]			RMSEV [mol/kg]		
	MEA	H ₂ O	CO ₂	MEA	H ₂ O	CO ₂
PLS 10-80%	0.0843	0.3265	0.0282	0.0958	0.3603	0.0300
PLS 10-80% w density	0.0770	0.2900	0.0255	0.0921	0.3314	0.0307
PLS 20-40%	0.0563	0.1949	0.0245	0.0772	0.2665	0.0296
PLS 20-40% w density	0.0519	0.1706	0.0233	0.0742	0.2524	0.0303

concentration and n number of samples.

2.3. Multivariate analysis and calibration

The PLS-R calibration models as well as prediction have all been calculated using the Unscrambler® X version 10.5 (CAMO Software). For PLS-R, the data were mean centered and calculated using the NIPALS algorithm. For validation of the calibration a cross validation with 10 random segments were applied. The used number of samples was 77 and the spectral range 895–1713 cm⁻¹. For some of the PLS-R models density was also included in the data set.

3. Results and discussion

3.1. Refined/extended calibration models

Density data may often be available online and the inclusion of density may yield an improved PLS-R model. The MEA calibration data set was extended with the corresponding densities. Prior to the PLS regression, the density data (kg/l) were scaled by the following

equation

$$\rho_{\text{Scaled}} = \frac{(\rho - 0.9)}{2} \quad (3)$$

In addition, the scaled density was transformed by the square root, similar to the FTIR intensities.

PLS calibration was also done with a narrowed concentration range for MEA, 20–40 wt% MEA. In that case 30 samples were included in the calibration calculation. The used wavelengths of the spectra were the same for all models. The models are denoted as follows:

- PLS 10–80 : Calibration based on the whole calibration set with MEA concentrations in the range from 10 to 80 wt%.set (77 samples)
- PLS 20–40 : Calibration based on MEA concentrations in the range from 20 to 40 wt% (30 samples)
- PLS 10–80 w density: Same dataset as used PLS 10–80, but here also the density is included in the model.
- PLS 20–40 w density: Same dataset as used in PLS 20–40, but here also the density is included in the model.

The RMSE is here used for comparison of the models and they are summarized in Table 2.

From Table 2 we see that there is a decrease in RMSEC when also density is included in the calibration. For RMSEV there is only a small reduction for MEA and H₂O when density is included, while for CO₂ the figures are pretty much the same.

4-(2-hydroxyethyl)-2-piperazinone (HEPO), N-(2-hydroxyethyl)-glycine (HeGly) and N,N'-bis(2-hydroxyethyl)-urea (MEA Urea) are major degradation products in MEA (Vevelstad et al., 2017). Based on this, a set of samples containing these compounds as well as diethanolamine (DEA) and NH₃ in 30% MEA were prepared. One subset with each compound was prepared with concentration in the range 0.1–1 wt

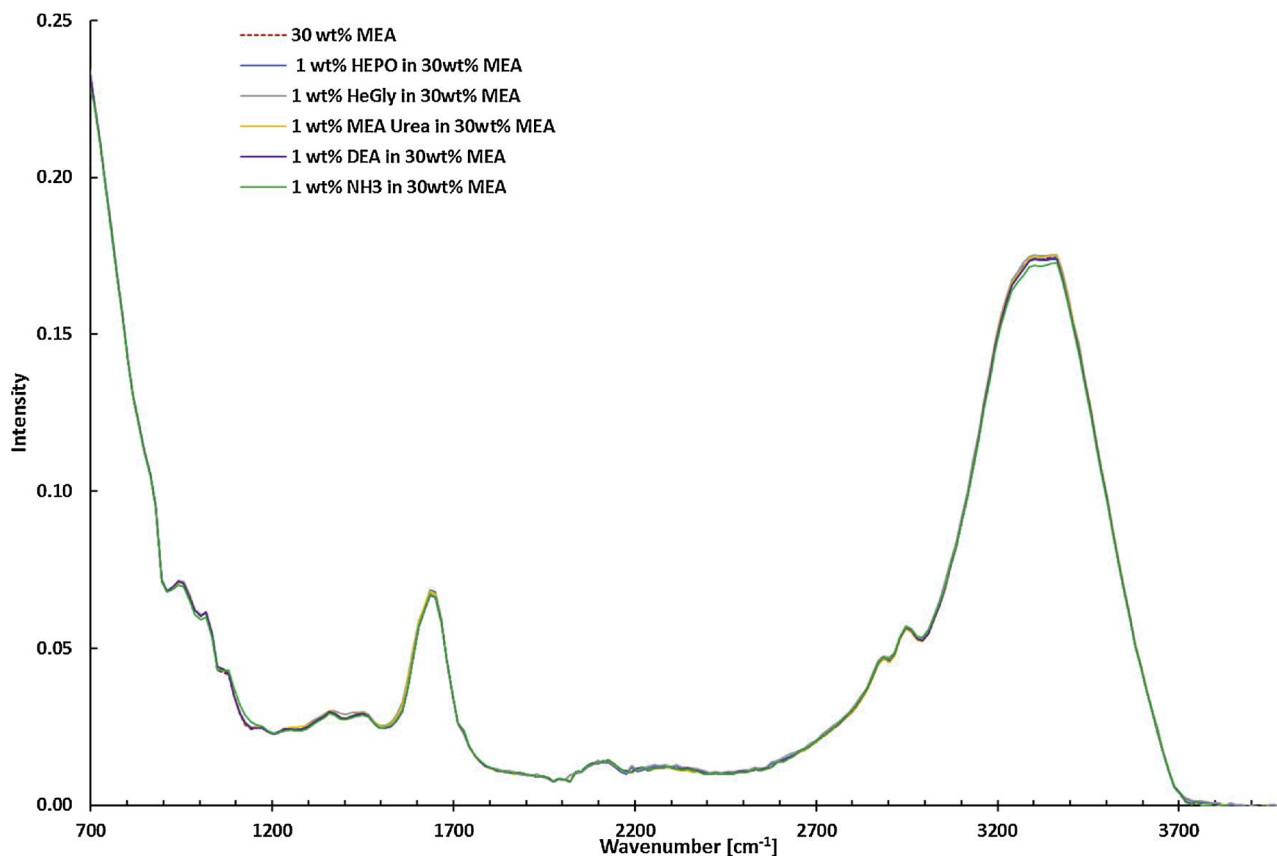


Fig. 1. Comparison of FTIR spectra of 30% MEA and 30% MEA with added 1 wt% of HEPO, HeGly, MEA Urea, DEA and NH₃.

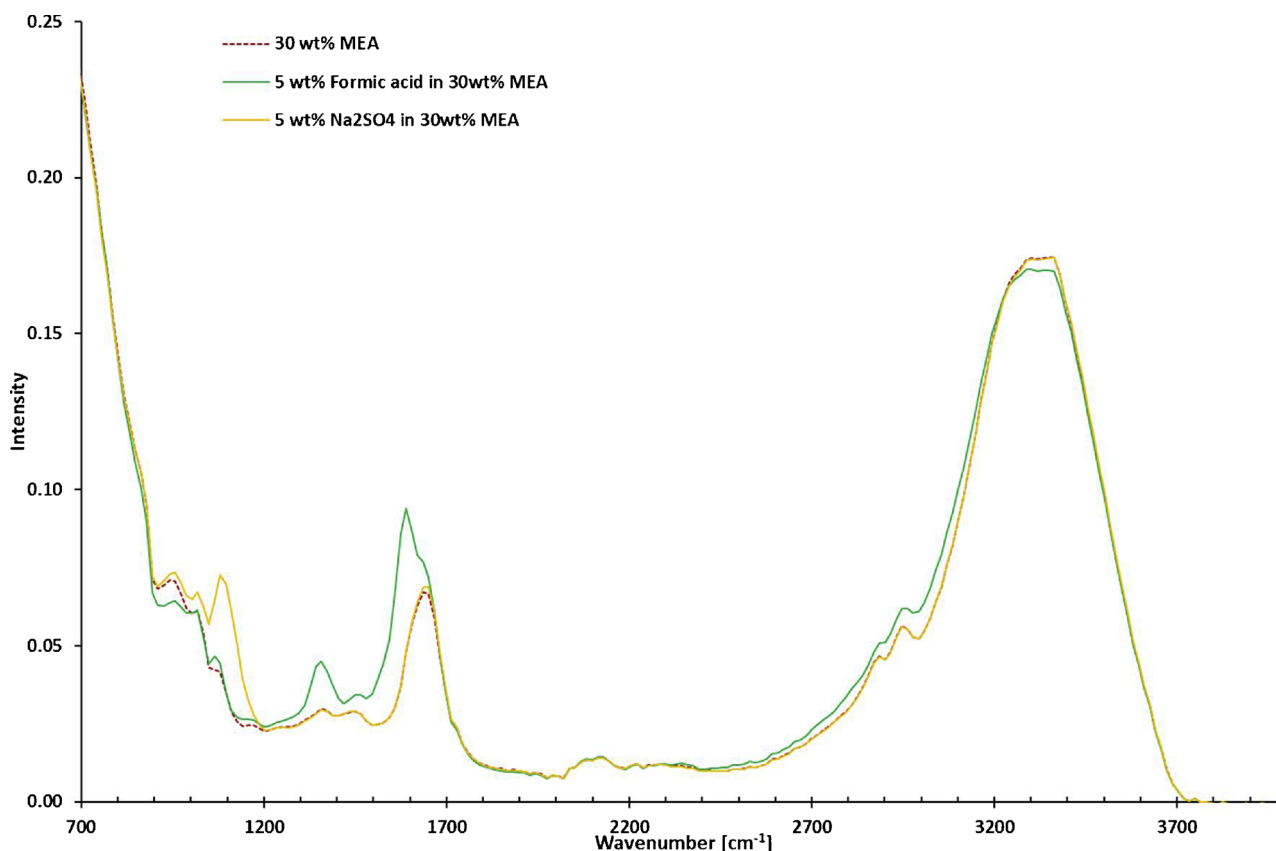


Fig. 2. Comparison of FTIR spectra of 30% MEA and 30% MEA with added 5 wt% formic acid and Na₂SO₄.

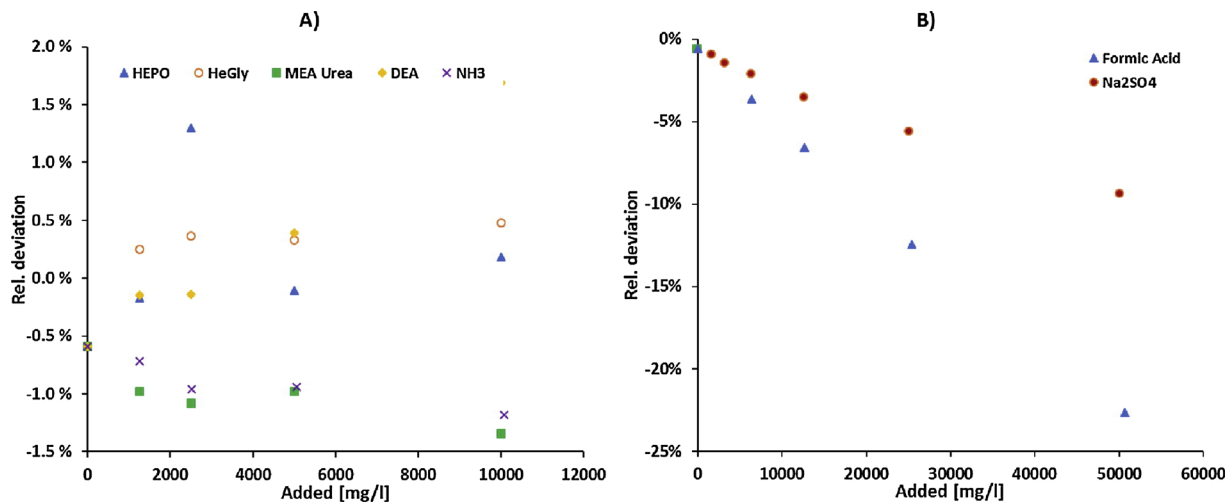


Fig. 3. Effect of added degradation products on prediction of MEA.

%). A calibration of these compounds was also tried, but as the sensitivity to these compounds (in this range) was low, no meaningful results were obtained.

Additionally, also subset with two HSS (heat stable salts), formate (added as formic acid) and sodium sulphate were prepared. For the subset with the HSS, the concentration range was extended to 5 wt%. A PLS calibration were calculated using an extended sample set (the HSS samples were added to the original calibration set), however the resulting RMSEC and RMSEV for all major compounds (MEA, CO₂ and H₂O) increased with several orders compared to the results in Table 2. A second approach were also tried, by first applying the PLS 10–80% on this set of subsamples and then using the residue spectres in a new PLS-

R model. The model was tested with one aged lean MEA sample, which was spiked with these compounds in the range of 0.5–5 wt% as well as with some heavily degraded MEA samples from oxidative degradation experiments. For sulphate, the obtained recovery was in the range from 60 to 230%, while for formate, the recovery was in the range of 85 to 270%. So, at this stage, these models yield more semi quantitative results for concentrations above 0.5 wt%

3.2. Effect of degradation products

As mention in the previous section HEPO, HeGly and MEA Urea are major degradation products in MEA. For HEPO, HeGly, MEA Urea, NH₃

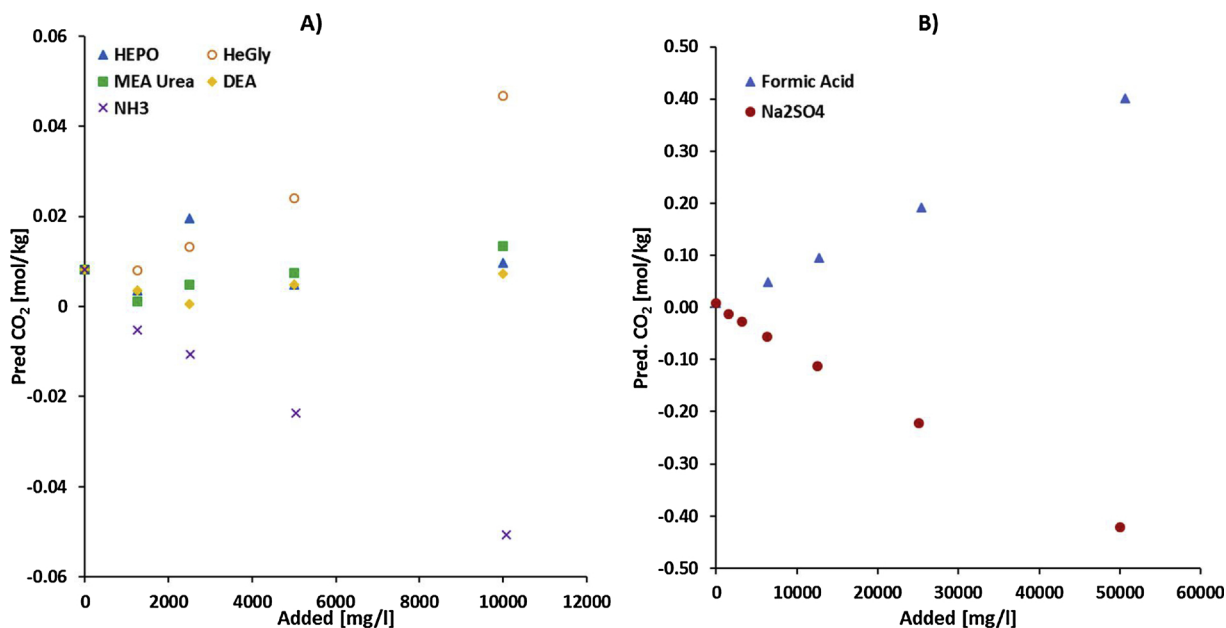


Fig. 4. Predicted CO₂ concentration in unloaded 30% MEA with addition of some degradation products.

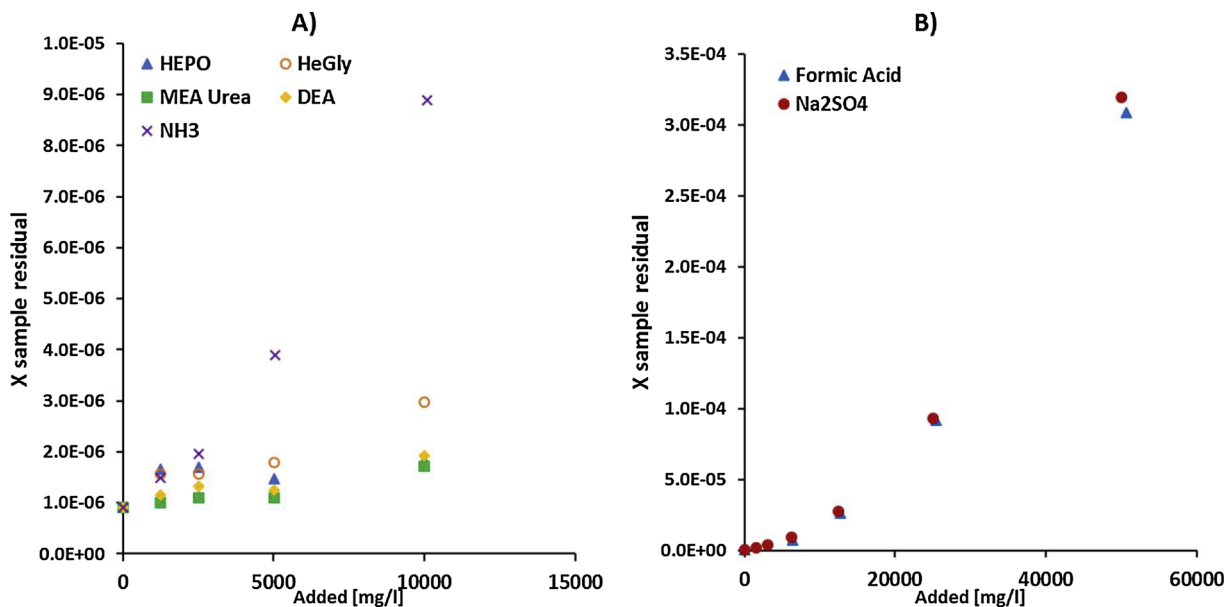


Fig. 5. Calculated X sample residuals for 30% MEA sample spiked with different degradation compounds.

Table 3

Samples from Oxidative degradation experiments. Experimental conditions different for each sample (temperature and O₂ content of gas). All samples are from end of experiment except for the first one (*na*=not analysed).

Sample	LC-MS MEA [mol/kg]	Titration Amine [mol/kg]	TIC/TOC CO ₂ [mol/kg]	IC Formate [mg/kg]	IC Sulphate [mg/kg]	Wet Chem. HSS [eq/kg]
75 °C 98%O ₂ t=0		4.50	1.78	39	1 067	<i>na</i>
75 °C 98%O ₂ t = 500 hrs	1.42	0.68	0.11	25 579	1 152	1.01
65 °C 49%O ₂ t = 670 hrs	2.18	1.73	0.68	9 975	<i>na</i>	0.59
75 °C 49%O ₂ t = 670 hrs	1.48	0.72	0.21	22 272	<i>na</i>	0.84
75 °C 6%O ₂ t = 860 hrs	3.23	2.98	1.06	6 109	2 414	0.23
55 °C 98%O ₂ t = 500 hrs	3.28	3.27	1.37	3453	2315	0.27
55 °C 49%O ₂ t = 500 hrs	3.68	3.56	1.49	2556	2563	0.19

Table 4

Predicted concentration based on PLS model 10–80% w density for samples from oxidative degradation experiments. Rel. Dev. is the relative deviation between the predicted and reference concentration.

Sample	MEA		CO ₂		H ₂ O
	C _{Pred} [mol/kg]	Rel. Dev.	C _{Pred} [mol/kg]	Rel. Dev.	
75 °C 98%O ₂ t = 0	4.55	1.1 %	1.834	3.0 %	35.6
75 °C 98%O ₂ t = 500 hrs	1.09	–23 %	0.782	611 %	49.9
65 °C 49%O ₂ t = 670 hrs	1.91	–12 %	1.160	71 %	46.2
75 °C 49%O ₂ t = 670 hrs	0.95	–36 %	0.802	282 %	50.4
75 °C 6%O ₂ t = 860 hrs	3.22	–0.4 %	1.316	24 %	41.4
55 °C 98%O ₂ t = 500 hrs	3.13	–4.4 %	1.602	17 %	41.0
55 °C 49%O ₂ t = 500 hrs	3.56	–3.3 %	1.697	14 %	39.3

and DEA, there was no or very little effect on the spectra with the addition of these compounds, as also illustrated in Fig. 1.

For the two HSS there were significant changes to the spectra when these were added as illustrated in Fig. 2.

To evaluate the influence of these degradation compounds on model's capability to predict MEA and CO₂, the deviation between predicted and reference concentrations was studied. The predicted value is here from the use of the PLS-R model PLS 10–80%. A plot of calculated relative deviations for the MEA concentration (i.e. relative difference between predicted and reference) for the different sub-sets are shown in Fig. 3.

As also the FTIR spectra illustrates, there are no or relatively small effect of the compounds HEPO, HeGly, MEA Urea, DEA and NH₃ on the prediction of MEA. However there seems to be a correlation between the amount of DEA in the solution and predicted MEA concentration, so DEA above 0.5 wt% may influence the predicted MEA concentration. For formate and Na₂SO₄ there is a significant influence on the predicted MEA concentration for concentration > 0.5 wt% and the effect increases with increasing concentration.

As these samples were CO₂-free (unloaded) the effect on CO₂ may be

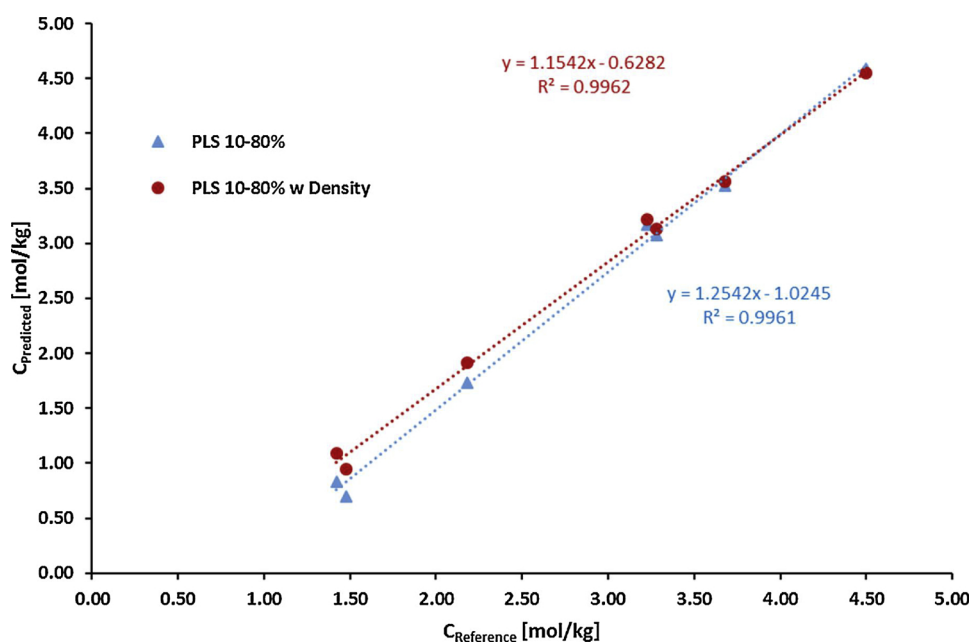


Fig. 6. Predicted MEA concentration of samples from oxidative degradation experiments obtained with two PLS-R models versus reference MEA concentration (LC–MS).

illustrated by looking at the predicted CO₂ concentration as shown in Fig. 4. For HEPO, HeGly, MEA Urea, DEA and NH₃ the effect is small (correspond to 2% relative or less for a typical Lean with CO₂ concentration of 1 mol/kg) for concentration below 0.5 wt%. The effect is also low at 1 wt% except for NH₃ and HeGly where the effect is minor (corresponds to around 5% relative for a typical lean with CO₂ concentration of 1 mol/kg).

For formate and sulphate, there is a significant effect when more than 0.5 wt% of these compounds are added. The effect seems to be opposite for these two compounds; formate causes an over prediction while sulphate causes an under prediction of CO₂ concentration.

When predicting results with the PLS model, also residuals (i.e. the part of the data that are not model, often denoted as X residuals) are calculated. Additionally, also sample residuals are calculated and the relation between the X residuals (E) and sample residuals is given in the equations below.

$$\text{Sample residual} = \text{MSE} = \frac{\text{RSS}}{N - f} = \frac{1}{N - f} \sum_{i=1}^n e_i^2 = \frac{1}{N - f} E^T E \quad (4)$$

Where:

$$E = X - \hat{X} \quad (5)$$

In Fig. 5 calculated sample residuals are plotted against added amount of the different compounds. For HEPO, HeGly, MEA Urea, DEA and NH₃ the information/trend is much the same as for the MEA deviation (Fig. 3) and predicted CO₂ concentrations (Fig. 4), small effect except for NH₃ and HeGly. For NH₃ and HeGly a significant increase can be observed with increasing concentration. Also for the other compounds there is a slight increase with concentration, especially above 0.5 wt%.

The presence of formic acid and Na₂SO₄ gives a clear increase in residuals as the added concentration increase. The development and the magnitude are very similar for both compounds. These results show that the residuals contain useful information and the results here indicate that they may also be used for monitoring HSS development.

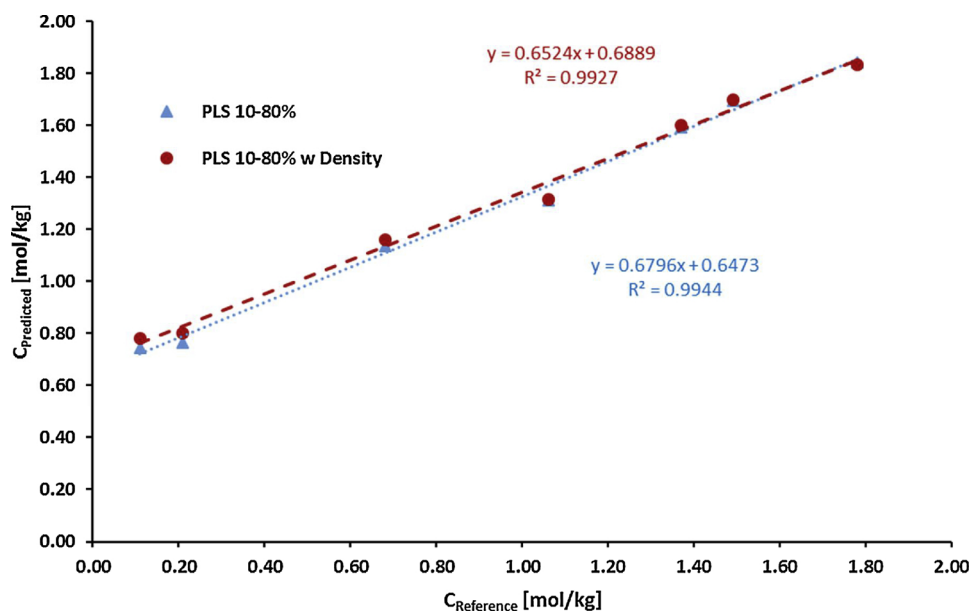


Fig. 7. Predicted CO₂ concentration of samples from oxidative degradation experiments obtained with two PLS-R models versus reference CO₂ concentration (TIC/TOC analyzer).

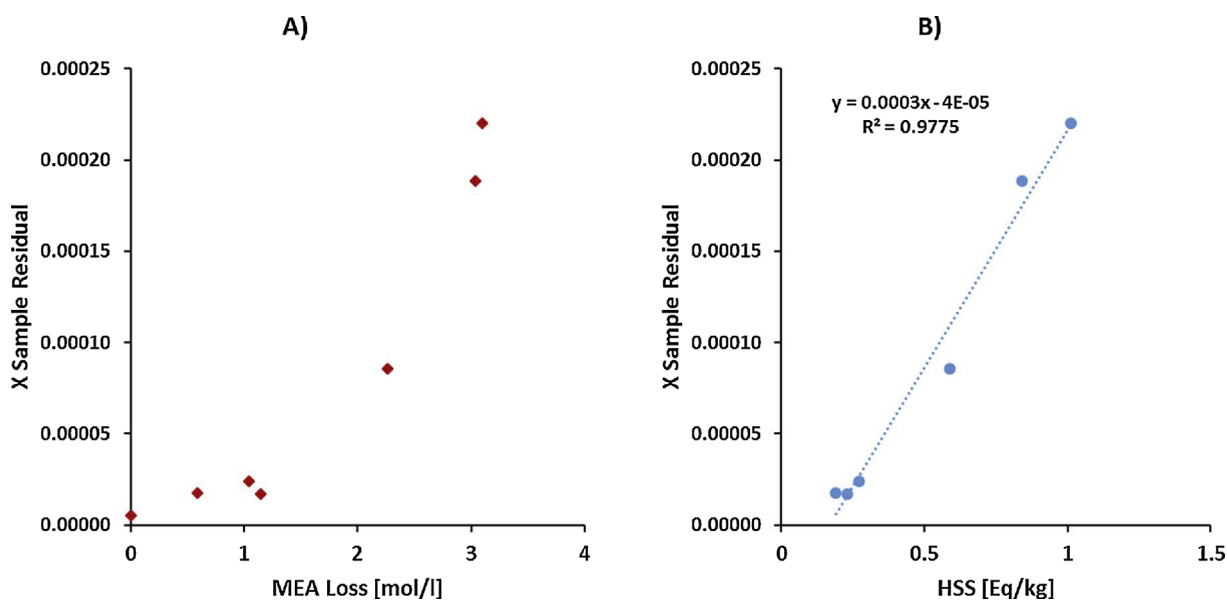


Fig. 8. Calculated X sample residuals for oxidative degradation samples as function of MEA loss and HSS content.

3.3. Test on real/aged samples

3.3.1. Oxidative degradation experiments at SINTEF

Some samples from earlier oxidative experiments at SINTEF has also been run on the FTIR. The oxidative degradation set-up consists of an open batch reactor (1 L) of glass where a recycle gas (blend of air/oxygen and CO₂) is sparged into the solution with circulation rate of about 50 L/h. More description of these samples and the set-up could be found in a paper by Vevelstad et al. (Vevelstad et al., 2016). For these samples the concentrations were calculated with two PLS-R models (PLS 10–80% and PLS 10–80% w density). An overview of the sample set and the reference concentrations of MEA and CO₂ as well as concentration of some HSS is summarized in Table 3. It must be noted that most of these samples are heavily degraded and probably we could not expect such degraded samples in a real pilot plant. However, it would be interesting to see how the PLS-R model will work on such samples.

Results from the prediction of concentration of these samples are

summarized in Table 4. The predicted results for MEA and CO₂ are also plotted against reference concentration in Figs. 6 and 7. As all these experiments started with the same MEA concentrations (4.55 mol/kg), the most degraded samples (and highest amount of HSS) has the lowest MEA concentration. As high levels of HSS causes increasing deviation in the predicted concentration the linear relation (see Figs. 6 and 7) between reference and predicted do not pass through origin.

From Table 4 we see that the predicted MEA concentration are pretty good (relative deviation below 5%) for all except three samples. For CO₂ there are large deviation for the same three samples, and also high deviation (20% relative) for the rest except for the first sample (start sample). As two of these samples contains high amounts of formate (around 2.5 wt%) and HSS, it is not surprising, based on the test with spiking, that the models yield high deviation for those samples.

From the plot for both MEA and CO₂ we see that both PLS models yield similar results (though the PLS 10–80% w density yields somewhat better results for the one with lowest MEA concentration).

Table 5

Predicted MEA concentration based on 4 different PLS-R models for samples from a MEA campaign in the SDR. RMSEP is root mean error of prediction. Rel. Dev. is the relative deviation between the predicted and reference concentration.

	Ref.MEA	PLS 10-80%		PLS 10-80% w density		PLS 20-40% w density		PLS 20-40%	
	[mol/kg]	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev
Lean 0 hrs	4.658	4.67	0.30 %	4.65	-0.26 %	4.64	-0.48 %	4.66	0.13 %
Lean 166 hrs	4.669	4.66	-0.13 %	4.64	-0.57 %	4.64	-0.64 %	4.66	-0.12 %
Lean 335 hrs	4.634	4.60	-0.68 %	4.58	-1.06 %	4.59	-1.03 %	4.61	-0.47 %
Lean 526 hrs	4.643	4.64	-0.14 %	4.62	-0.52 %	4.62	-0.46 %	4.65	0.11 %
Lean 694 hrs	4.603	4.54	-1.37 %	4.53	-1.57 %	4.54	-1.34 %	4.56	-0.89 %
Lean 845 hrs	4.635	4.58	-1.10 %	4.57	-1.45 %	4.58	-1.19 %	4.61	-0.61 %
Lean 860 hrs	4.596	4.55	-0.92 %	4.55	-1.10 %	4.56	-0.87 %	4.58	-0.46 %
Lean 861 hrs	4.527	4.54	0.26 %	4.51	-0.29 %	4.52	-0.17 %	4.55	0.61 %
Rich 166 hrs	4.419	4.38	-0.87 %	4.34	-1.82 %	4.47	1.19 %	4.54	2.70 %
Rich 335 hrs	4.383	4.31	-1.76 %	4.27	-2.59 %	4.42	0.75 %	4.48	2.27 %
Rich 526 hrs	4.435	4.38	-1.21 %	4.34	-2.06 %	4.48	1.02 %	4.54	2.47 %
Rich 694 hrs	4.383	4.31	-1.69 %	4.28	-2.41 %	4.43	0.99 %	4.49	2.36 %
Rich 860 hrs	4.388	4.27	-2.65 %	4.24	-3.31 %	4.40	0.21 %	4.46	1.54 %
RMSEP		0.055		0.077		0.040		0.065	

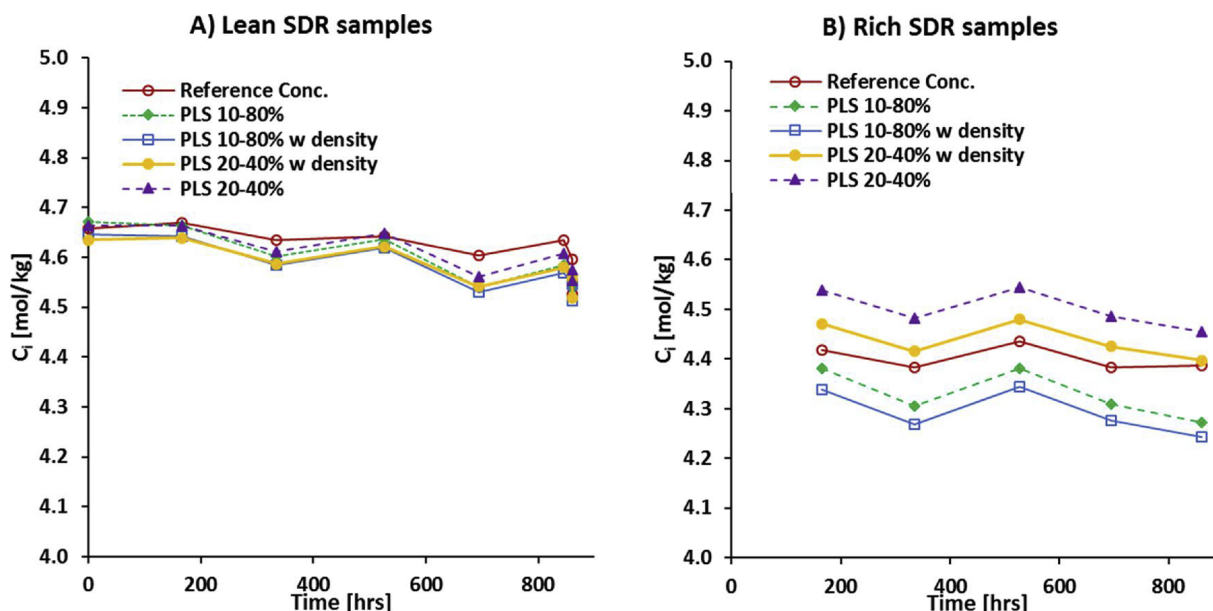


Fig. 9. Predicted MEA concentration in Lean and Rich samples obtained using 4 different PLS-R models.

Table 6

Predicted CO₂ concentration based on 4 different PLS-R models for samples from a MEA campaign in the SDR. RMSEP is root mean error of prediction. Rel. Dev. is the relative deviation between the predicted and reference concentration.

	Ref.CO ₂	PLS 10-80%		PLS 10-80% w density		PLS 20-40% w density		PLS 20-40%	
	[mol/kg]	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev
Lean 0 hrs	1.034	1.074	3.92 %	1.069	3.43 %	1.074	3.85 %	1.076	4.04 %
Lean 166 hrs	0.994	1.036	4.16 %	1.032	3.75 %	1.037	4.31 %	1.038	4.37 %
Lean 335 hrs	0.991	1.042	5.13 %	1.039	4.79 %	1.041	5.08 %	1.043	5.26 %
Lean 526 hrs	1.029	1.095	6.39 %	1.091	6.03 %	1.094	6.33 %	1.096	6.52 %
Lean 694 hrs	0.964	1.022	6.05 %	1.020	5.83 %	1.024	6.24 %	1.025	6.28 %
Lean 845 hrs	1.021	1.080	5.72 %	1.076	5.34 %	1.080	5.79 %	1.082	5.97 %
Lean 860 hrs	0.990	1.056	6.70 %	1.054	6.50 %	1.059	6.97 %	1.059	6.94 %
Rich 166 hrs	2.157	2.131	-1.22 %	2.120	-1.74 %	2.159	0.07 %	2.199	1.92 %
Rich 335 hrs	2.055	2.106	2.48 %	2.096	1.99 %	2.134	3.83 %	2.174	5.79 %
Rich 526 hrs	2.132	2.128	-0.19 %	2.117	-0.68 %	2.155	1.09 %	2.194	2.91 %
Rich 694 hrs	2.093	2.111	0.83 %	2.101	0.37 %	2.141	2.29 %	2.180	4.12 %
Rich 860 hrs	2.107	2.106	-0.07 %	2.097	-0.50 %	2.139	1.49 %	2.176	3.28 %
RMSEP		0.046		0.043		0.052		0.068	

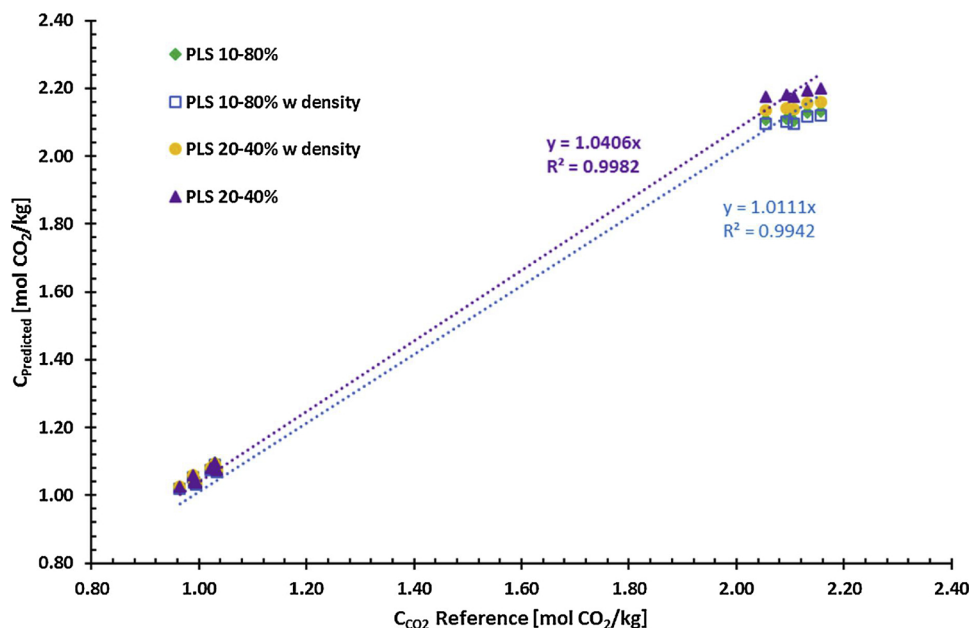


Fig. 10. Predicted CO₂ concentration of SDR samples obtained by 4 PLS-R models versus reference concentration.

Table 7

Predicted H₂O concentration based on 4 different PLS-R models for samples from a MEA campaign in the SDR. RMSEP is root mean error of prediction. Rel. Dev. is the relative deviation between the predicted and reference concentration.

	Ref. H ₂ O [mol/kg]	PLS 10-80%		PLS 10-80% w density		PLS 20-40% w density		PLS 20-40%	
		C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev
Lean 0 hrs	37.6	37.1	−1.3 %	37.2	−1.0 %	37.2	−0.93 %	37.1	−1.2 %
Lean 166 hrs	37.5	37.2	−0.78 %	37.3	−0.57 %	37.3	−0.57 %	37.2	−0.80 %
Lean 335 hrs	37.9	37.4	−1.3 %	37.5	−1.1 %	37.5	−1.1 %	37.4	−1.4 %
Lean 526 hrs	36.6	37.2	1.7 %	37.2	1.8 %	37.2	1.8 %	37.1	1.5 %
Lean 694 hrs	37.0	37.7	1.9 %	37.7	2.0 %	37.7	1.8 %	37.6	1.6 %
Lean 860 hrs	36.6	37.5	2.6 %	37.6	2.7 %	37.5	2.6 %	37.5	2.4 %
Lean 861 hrs	36.3	36.5	0.62 %	36.6	0.90 %	36.6	0.81 %	36.5	0.44 %
Rich 166 hrs	35.4	35.5	0.15 %	35.7	0.63 %	35.1	−0.91 %	34.8	−1.8 %
Rich 335 hrs	36.2	35.8	−0.97 %	36.0	−0.56 %	35.4	−2.2 %	35.0	−3.1 %
Rich 526 hrs	34.8	35.5	2.0 %	35.6	2.5 %	35.1	0.86 %	34.8	−0.04 %
Rich 694 hrs	35.0	35.8	2.2 %	35.9	2.6 %	35.3	0.84 %	35.0	−0.01 %
Rich 860 hrs	34.8	35.9	3.4 %	36.0	3.7 %	35.4	1.9 %	35.1	1.1 %
	RMSEP	0.640		0.690		0.545		0.566	

For these extremely degraded samples it would be interesting to see if there is any correlation between the sample residuals and MEA loss or HSS amount for these samples. In Fig. 8 the residuals are plotted against MEA loss and also against HSS concentration. The MEA loss is here simply set as 4.55 (start conc.) minus the actual MEA concentration given in Table 3. We see that there is a clear increase in residuals with increasing MEA loss and a fairly linear trend when the residuals are plotted against the HSS concentration.

3.3.2. SDR campaign at SINTEF

Also a set of MEA samples from a campaign in SINTEF's solvent degradation rig (SDR) were analysed and predicted with the PLS-R models. The SDR is a lab scale degradation apparatus capable of predicting degradation at real-life process conditions. The rig has continuous cycling of solvent between a simulated absorber- and stripper section, with realistic temperature, CO₂ loading and residence time of the solvent. In the absorber section, the solvent is contacted with synthetic flue gas mixtures with options for addition of NO_x or other compounds. The SDR is built for continuous operation, with typical test campaigns duration of 5 weeks (Einbu et al., 2013).

The predicted MEA concentrations from the different PLS models are summarized in Table 5.

All models show good agreement for MEA versus the reference concentrations, in this case the model PLS 20–40% w density shows the lowest RMSEP, and for this model almost all relative deviations are below 1% relative.

A graphical comparison for the lean and rich samples is given in Fig. 9. We see that for the lean samples all models predict slightly lower than the reference concentration, but all show the same trend with time. For the rich samples, deviation is slightly higher than for the lean, here the two models where also density data is included yields higher results than the reference, while the models without density yields lower results than the reference.

In Table 6 the predicted results for CO₂ are summarized. For CO₂ the relative deviations are higher than for MEA. The model PLS 10–80% w density yields the lowest RMSEP, but the value for PLS 10–80% is only slightly higher.

The predicted CO₂ concentrations are also plotted versus the reference concentrations in Fig. 10. As this campaign was run to maintain a fairly constant lean and rich CO₂ loading, the CO₂ groups around two concentration levels (1 mol/kg for Lean and around 2 mol/kg for Rich) with little span within each group. The predicted concentrations for all models give very similar values for the lean samples while there is more difference for the rich samples.

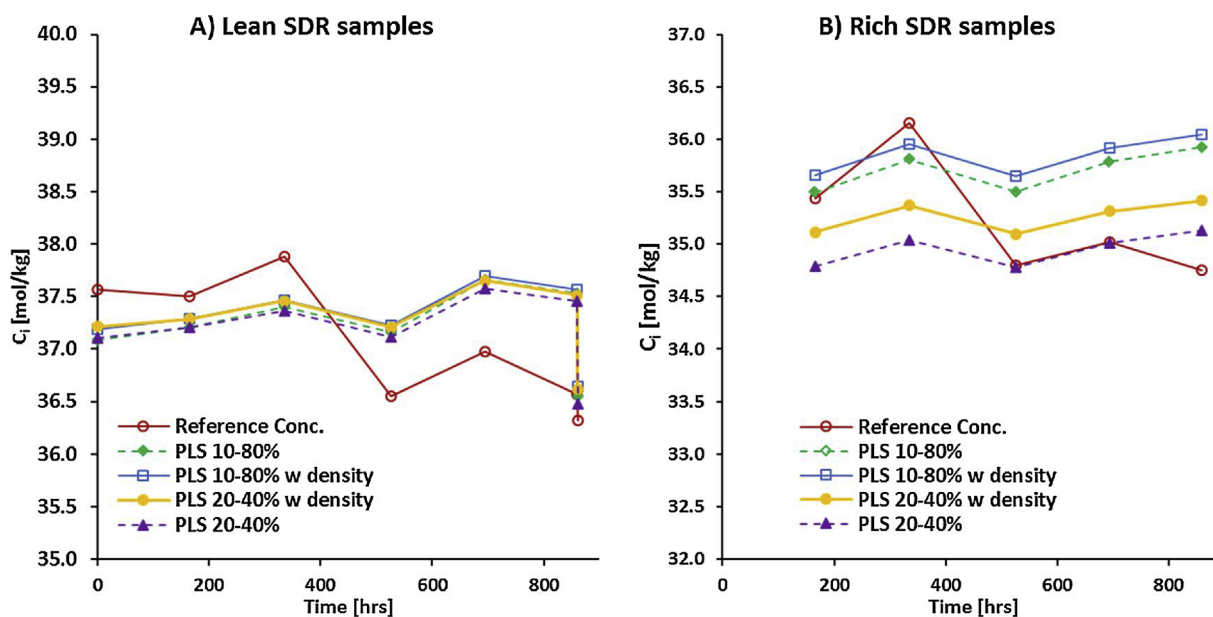


Fig. 11. Predicted H_2O concentration in Lean and Rich samples obtained using 4 different PLS models.

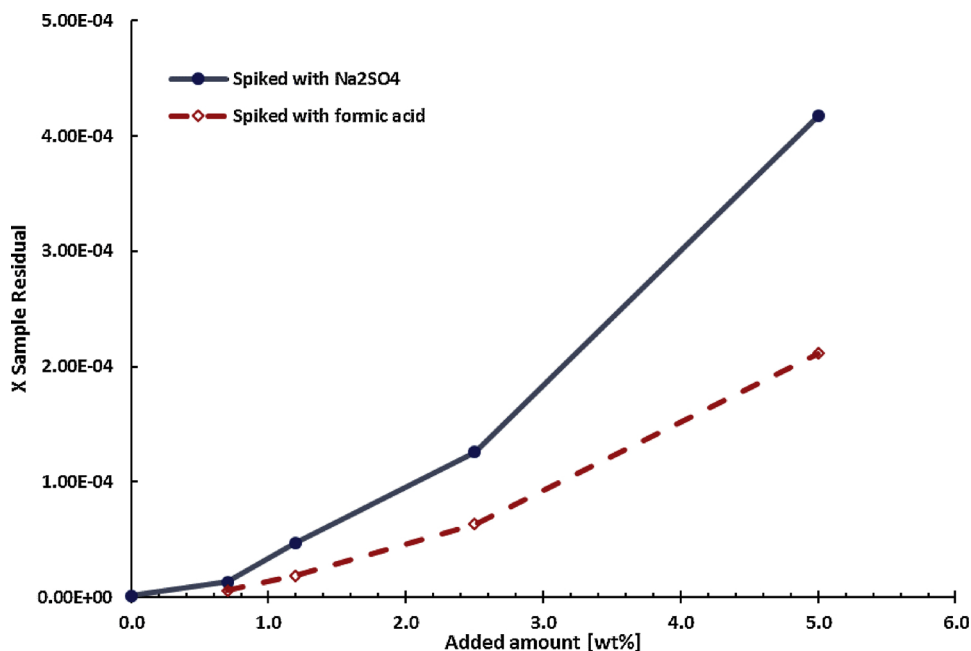


Fig. 12. Calculated X sample residuals for Lean MEA sample spiked with formic acid and Na_2SO_4 .

Finally, the predicted results for H_2O is summarized in Table 7. For this set, all models agree well with the reference concentrations with relative deviation mainly below 2%. In this case the models with the reduced sample set yield the lowest RMSEP.

The results for H_2O are also shown graphically in Fig. 11. We see that all models' yields were similar results for the lean samples while there some more difference for the rich samples

As these samples had a very low level of HSS, one of the latest lean samples were used to produce a set of spiked samples with Na_2SO_4 and formic acid. This was done to study if the effect of HSS shows similar trend on an CO_2 loaded and aged samples as the fresh and unloaded MEA. The calculated sample residuals for these spiked samples is shown versus added amount in Fig. 12. The residuals were from the model PLS 10–80%. Also here a clear increase in residuals with increasing amount of added formic acid and Na_2SO_4 is observed. In this case the residuals

are higher with the addition Na_2SO_4 than formate (with unloaded fresh MEA they were very similar)

The sample residual for the lean samples were also calculated and they are shown as function of time in Fig. 13. Except for the starting samples there is an increase in the residual during the campaign, and this increase may be interpreted as increased degradation of the solvent

3.3.3. Samples from pilot plant campaign at Tiller

A set of Lean samples from an MEA campaign at SINTEF Tiller pilot plant was analysed with FTIR and the concentrations were predicted using the PLS models. The SINTEF CO_2 capture pilot facility at Tiller has flexibility regarding the flue gas source, with pilot plants operating on flue gas from either a propane burner or from a coal/biomass burner. The solvents analysed were operated in a full height pilot plant (20 m height absorber section with Mellapak 2X structured packings)

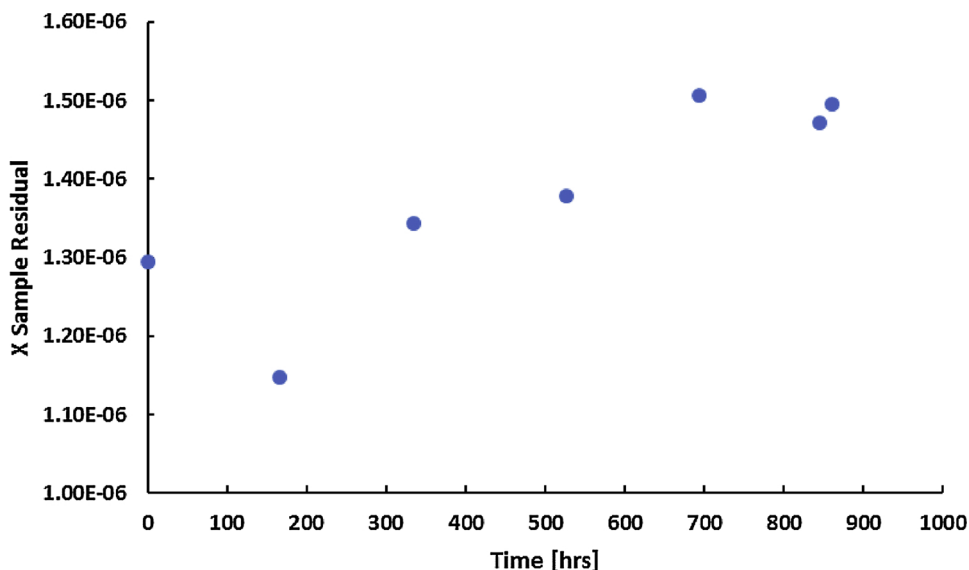


Fig. 13. Calculated X sample residuals for the Lean MEA samples.

Table 8

Predicted MEA concentration based on 4 different PLS-R models for Lean samples from MEA campaign at Tiller. RMSEP is root mean error of prediction. Rel. Dev. is the relative deviation between the predicted and reference concentration.

	Ref. MEA [mol/kg]	PLS 10-80%		PLS 10-80% w density		PLS 20-40% w density		PLS 20-40%	
		C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev
Lean 50hrs	4.52	4.55	0.78 %	4.54	0.58 %	4.58	1.35 %	4.61	2.12 %
Lean 220hrs	4.45	4.40	-1.14 %	4.42	-0.68 %	4.43	-0.60 %	4.43	-0.64 %
Lean 410hrs	4.52	4.30	-4.85 %	4.33	-4.10 %	4.36	-3.45 %	4.35	-3.61 %
Lean 650hrs	4.43	4.14	-6.42 %	4.17	-5.80 %	4.16	-6.08 %	4.14	-6.36 %
Lean 890hrs	4.18	4.05	-2.96 %	4.09	-2.00 %	4.09	-2.12 %	4.06	-2.83 %
Lean 900hrs	3.73	3.62	-2.97 %	3.74	0.44 %	3.76	0.82 %	3.64	-2.35 %
Lean 1420hrs	4.40	4.36	-0.85 %	4.42	0.43 %	4.43	0.68 %	4.39	-0.12 %
Lean 1710hrs	4.61	4.54	-1.49 %	4.63	0.41 %	4.68	1.55 %	4.62	0.28 %
Lean 1930 hrs	4.39	4.46	1.74 %	4.53	3.27 %	4.66	6.26 %	4.66	6.11 %
RMSEP		0.138		0.120		0.146		0.153	

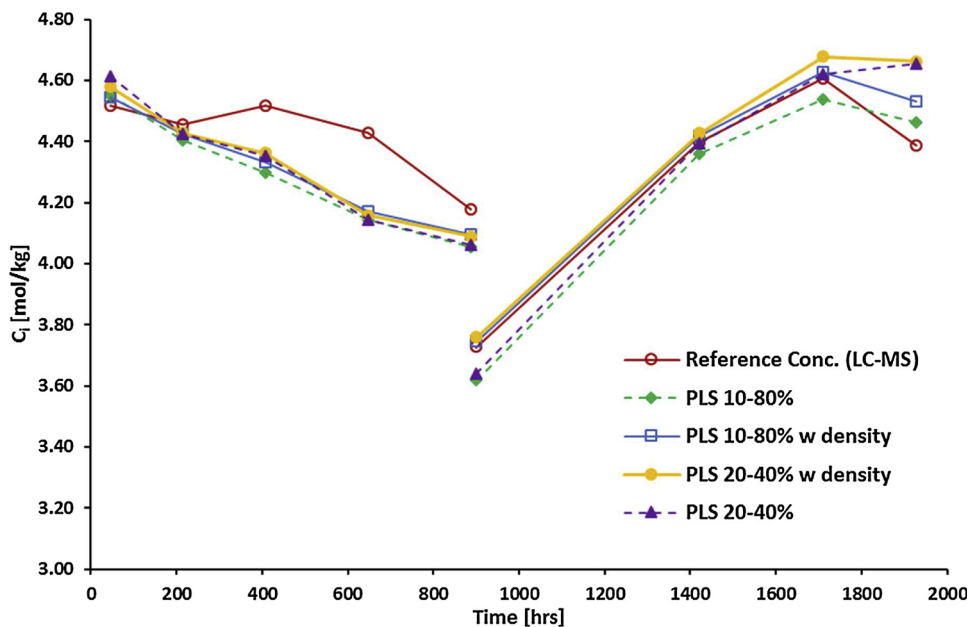


Fig. 14. Predicted and reference MEA concentration for Lean Tiller samples obtained by the different PLS-R models.

Table 9

Predicted CO₂ concentration based on 4 different PLS-R models for Lean samples from MEA campaign at Tiller. RMSEP is root mean error of prediction. Rel. Dev. is the relative deviation between the predicted and reference concentration.

	Ref. CO ₂ [mol/kg]	PLS 10-80%		PLS 10-80% w density		PLS 20-40% w density		PLS 20-40%	
		C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev
Lean 50hrs	0.912	0.96	5.79 %	0.96	5.77 %	0.96	5.20 %	0.97	6.33 %
Lean 220hrs	0.672	0.67	-0.32 %	0.68	0.50 %	0.67	-0.34 %	0.66	-1.20 %
Lean 410hrs	0.676	0.65	-3.96 %	0.66	-2.73 %	0.65	-3.29 %	0.65	-4.16 %
Lean 650hrs	0.755	0.75	-0.32 %	0.76	0.39 %	0.75	-0.18 %	0.74	-1.83 %
Lean 890hrs	0.699	0.67	-4.09 %	0.68	-2.97 %	0.68	-2.72 %	0.66	-5.31 %
Lean 900hrs	0.567	0.51	-9.45 %	0.54	-4.67 %	0.55	-2.49 %	0.51	-10.7 %
Lean 1420hrs	0.857	0.85	-1.28 %	0.86	0.02 %	0.86	0.31 %	0.84	-2.19 %
Lean 1710hrs	0.613	0.64	3.80 %	0.65	6.69 %	0.66	8.21 %	0.64	3.93 %
RMSEP		0.031		0.027		0.027		0.036	

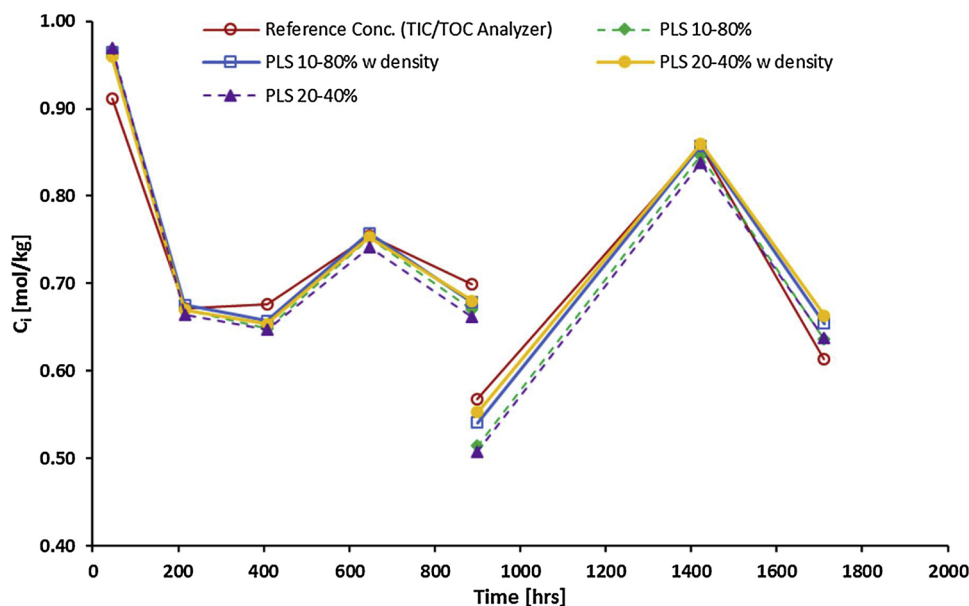


Fig. 15. Predicted and reference CO₂ concentration for Lean Tiller samples obtained by the different PLS-R models.

Table 10

Predicted H₂O concentration based on 4 different PLS-R models for Lean samples from MEA campaign at Tiller. RMSEP is root mean error of prediction. Rel. Dev. is the relative deviation between the predicted and reference concentration.

	Ref. H ₂ O [mol/kg]	PLS 10-80%		PLS 10-80% w density		PLS 20-40% w density		PLS 20-40%	
		C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev	C _{Pred}	Rel. Dev
Lean 50hrs	36.9	37.8	2.4 %	37.8	2.5 %	37.7	2.2 %	37.5	1.8 %
Lean 220hrs	37.8	39.0	3.2 %	38.9	3.0 %	38.9	3.0 %	38.9	3.0 %
Lean 410hrs	36.3	39.4	8.4 %	39.3	8.0 %	39.2	7.8 %	39.2	7.9 %
Lean 650hrs	37.0	39.7	7.1 %	39.6	6.8 %	39.6	7.0 %	39.7	7.2 %
Lean 890hrs	37.7	40.2	6.5 %	40.0	6.1 %	40.0	6.1 %	40.2	6.5 %
Lean 1420hrs	36.0	38.7	7.5 %	38.5	6.9 %	38.4	6.8 %	38.6	7.3 %
Lean 1710hrs	34.8	38.6	11 %	38.4	10 %	38.1	9.5 %	38.3	10 %
Lean 1930 hrs	33.8	37.9	12 %	37.6	11 %	37.2	9.8 %	37.2	9.9 %
RMSEP		2.8		2.6		2.5		2.6	

operated with propane burner flue gas and an electric reboiler. The plant is constructed with 316SS stainless steel for all parts in contact with solvent and flue gas. Further details of the Tiller pilot plant are given by Mejdell and co-workers (Mejdell et al., 2011). The samples from the Tiller were from two different campaigns; the first campaign was from an approximately 900 hrs operation. The used solvent was stored for approximately 10 months before it was re-used in a second campaign. In the latter test campaign some fresh MEA was added as make-up around 1000 hrs. In Table 8 the predicted MEA concentrations for the 4 PLS-R models are summarized.

Based on the calculated RMSEP, the model *PLS 10-80% w density* yields the best results. The obtained results are also shown graphically in Fig. 14. We see that all models produce results that follows the same trend. Except for the two samples at 410 and 650 hrs there are very good agreement between the predicted and reference concentrations.

Similarly, the predicted concentrations of CO₂ for the 4 PLS-R models are summarized in Table 9 and the results are also illustrated graphically in Fig. 15. Also for CO₂ *PLS 10-80% w density* seems to give the best results (lowest RMSEP) though the *PLS 20-40% w density* give the same results and *PLS 10-80%* only slightly higher RMSEP. For these

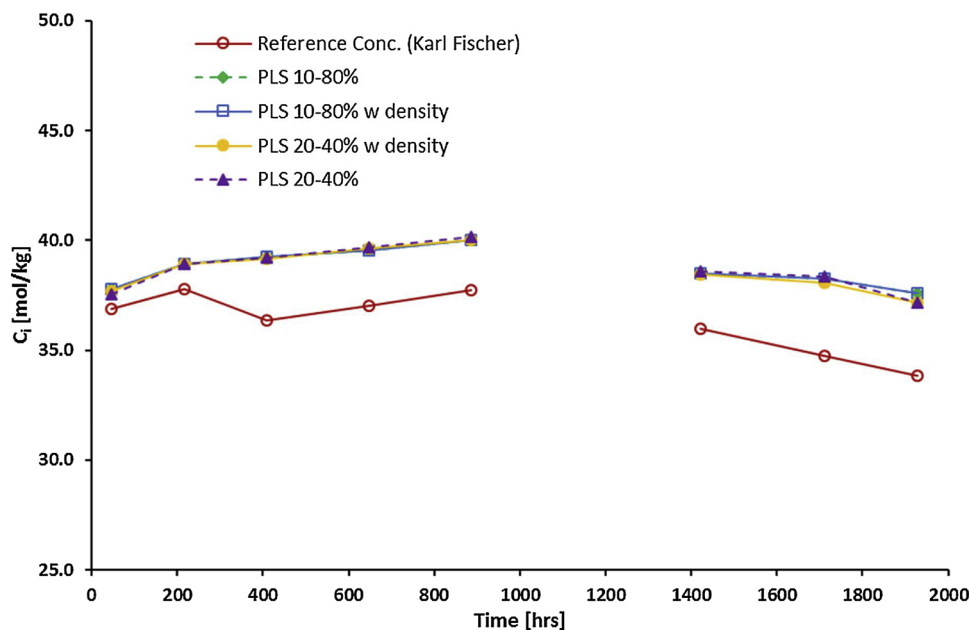


Fig. 16. Predicted H₂O concentration for Lean samples for the different PLS-R models.

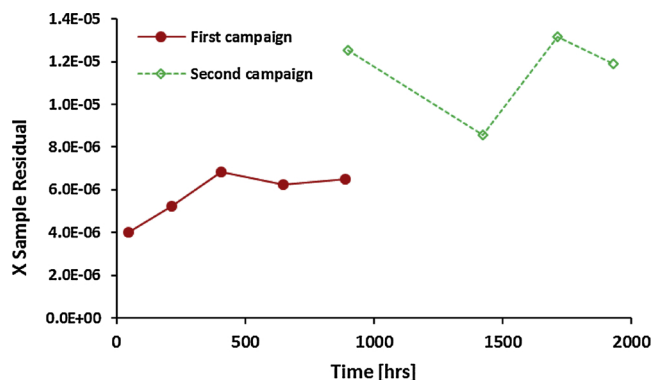


Fig. 17. Calculated X sample residuals for Lean MEA sample from Tiller campaign.

Table 11

Samples from MEA campaign at TCM. Concentrations and density provided by TCM DA, Tot Alk is total alkalinity determined by titration, MEA is determined by Gas Chromatography, CO₂ by TIC/TOC analyzer and density from online measurement.

Sample id	Tot Alk [mol/kg]	MEA [mol/kg]	CO ₂ [mol/kg]	Density [kg/m ³]
Lean 04/09-17	4.7	4.741	0.847	1058
Lean 11/09-17	5.1	5.238	1.005	1072
Lean 18/09-17	4.7	4.866	0.788	1070
Lean 25/09-17	4.6	4.551	0.934	1088
Lean 02/10-17	4.9	4.941	1.088	1095
Lean 09/10-17	4.7	4.878	1.074	1101
Rich 04/09-17	4.25	4.279	2.321	1106
Rich 11/09-17	4.64	4.768	2.453	1119
Rich 02/10-17	4.71	4.675	2.153	1121
Rich 09/10-17	4.51	4.438	2.132	1128

models, there is also good agreement with the reference concentrations. The last lean sample (Lean 1930 hrs) is omitted in the calculations of RMSEP as the results from FTIR is consider as an outlier (all models give almost the same results with a deviation of above 20% relative). Except for the last sample all models show good agreement with the reference concentrations.

Finally, the predicted concentrations of H₂O for the 4 PLS-R models are summarized in Table 10 and the results are also illustrated graphically in Fig. 16. For H₂O the lean sample at 900 hrs is omitted as the H₂O results from Karl Fischer analysis is not available. For H₂O all models yield nearly the same RMSEP and the predicted concentration are very similar for all the samples. In this case the predicted results are higher than the reference concentration for all the samples and the relative deviation is higher than for MEA and CO₂. Why the prediction of H₂O is poorer for this sample set is not clearly understood, one reason could be some unknown contaminants in the solvent, but this is not verified. The predicted H₂O concentration follows much the same trend as the reference and reflects the changes in the H₂O concentration but with a systematic to high concentration (i.e. poorer accuracy). This demonstrates that a good practice will be to include dedicate off-line analysis of some samples for control when a new campaign is started.

As mentioned in the previous sections, sample residuals may contain useful information. In Fig. 17 a plot of the calculated sample residuals versus time for these lean MEA samples is shown. The residuals are from the model PLS 10–80% w density. From Fig. 17 we see an increase in residuals for the first part of the first campaign, then they are nearly constant for the rest of the campaign. For the second campaign the residuals are higher, which may indicate some degradation due to storage. Lower residuals (at approximately 1400 and 1900 hrs.) corresponds to the addition of fresh MEA.

3.3.4. Samples from MEA campaign at TCM

A set of samples from an MEA campaign at Technology Center Mongstad (TCM) was also analyzed with FTIR and concentrations predicted with the PLS models. The capture plant at TCM is large scale solvent based CO₂ capture demo facility constructed by Aker Solutions. The design capacity is 80–200 ton CO₂ per day and is operated with an exhaust gas with 3.5–15% CO₂ content from either the Combined Heat 398 and Power plant (CHP) at Mongstad or from the Residue Fluid Catalytic Cracker (RFCC) plant at Mongstad refinery.

The TCM test campaign was started in June 2017 and the tested samples here were from the period 4th of September until the 9th of October 2017 (Morken et al., 2019). The samples with corresponding analysis results for MEA, CO₂ and density has been provided by TCM DA and they are summarized in Table 11.

The obtained results using FTIR spectra and densities using the different PLS-R models are given in Tables 12 and 13 for MEA and CO₂

Table 12

Predicted MEA concentration based on 4 different PLS-R models for samples from MEA campaign at TCM. RMSEP is root mean error of prediction. Rel. Dev. is the relative deviation between the predicted and reference concentration.

Sample id	PLS 10-80%		PLS 10-80% w density		PLS 20-40%		PLS 20-40% w density	
	[mol/kg]	Rel. Dev.	[mol/kg]	Rel. Dev.	[mol/kg]	Rel. Dev.	[mol/kg]	Rel. Dev.
Lean 04/09-17	4.76	0.3 %	4.80	1.2 %	4.85	2.2 %	4.81	1.4 %
Lean 11/09-17	5.40	3.0 %	5.46	4.2 %	5.47	4.3 %	5.43	3.7 %
Lean 25/09-17	5.06	4.0 %	5.16	6.1 %	5.15	5.8 %	5.14	5.5 %
Lean 02/10-17	4.99	1.0 %	5.12	3.6 %	5.21	5.3 %	5.20	5.2 %
Lean 09/10-17	4.76	-2.3 %	4.91	0.6 %	4.99	2.2 %	4.97	2.0 %
Rich 04/09-17	4.16	-2.8 %	4.13	-3.4 %	4.52	5.6 %	4.37	2.1 %
Rich 11/09-17	4.65	-2.5 %	4.62	-3.1 %	5.03	5.4 %	4.85	1.8 %
Rich 02/10-17	4.83	3.2 %	4.82	3.1 %	5.17	11 %	4.99	6.7 %
Rich 09/10-17	4.46	0.5 %	4.49	1.3 %	4.91	11 %	4.75	7.0 %
RMSEP	0.120		0.163		0.300		0.211	

Table 13

Predicted CO₂ concentration based on 4 different PLS-R models for samples from MEA campaign at TCM. RMSEP is root mean error of prediction. Rel. Dev. is the relative deviation between the predicted and reference concentration.

Sample id	PLS 10-80%		PLS 10-80% w density		PLS 20-40%		PLS 20-40% w density	
	[mol/kg]	Rel. Dev.	[mol/kg]	Rel. Dev.	[mol/kg]	Rel. Dev.	[mol/kg]	Rel. Dev.
Lean 04/09-17	0.922	8.9 %	0.932	10 %	0.890	5.1 %	0.882	4.1 %
Lean 11/09-17	1.10	9.0 %	1.11	10 %	1.05	4.2 %	1.04	3.6 %
Lean 25/09-17	0.96	21 %	0.98	24 %	0.896	14 %	0.899	14 %
Lean 02/10-17	1.33	22 %	1.36	25 %	1.29	18 %	1.29	18 %
Lean 09/10-17	1.43	33 %	1.46	36 %	1.38	28 %	1.37	28 %
Rich 04/09-17	2.14	-7.9 %	2.13	-8.3 %	2.20	-5.1 %	2.12	-8.6 %
Rich 11/09-17	2.35	-4.4 %	2.34	-4.7 %	2.40	-2.3 %	2.31	-6.0 %
Rich 02/10-17	2.31	7.1 %	2.30	6.9 %	2.31	7.2 %	2.23	3.4 %
Rich 09/10-17	2.33	9.3 %	2.33	9.5 %	2.36	11 %	2.27	6.6 %
RMSEP	0.192		0.207		0.163		0.160	

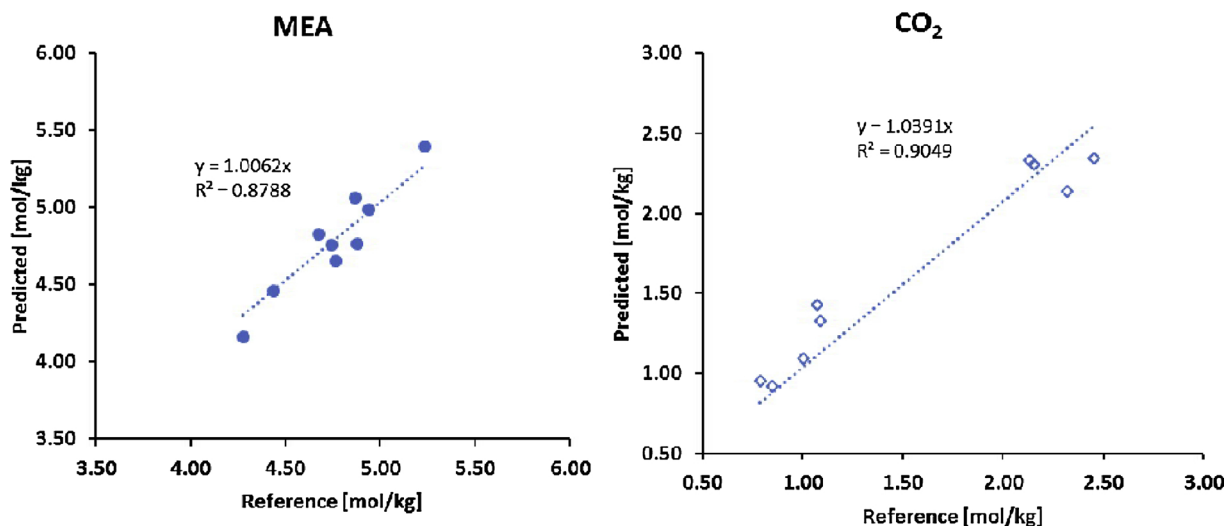


Fig. 18. Predicted versus reference concentration of MEA and CO₂ for samples from campaign at TCM.

respectively.

For MEA all models give good predictions, with the model PLS 10–80 having the lowest RMSEP. With this model all results are within $\pm 4\%$ relative compared to the reference concentration, the magnitude of RMSEP is also very similar to the results obtained for the Tiller samples. For CO₂ the results are not as good as for MEA, here deviation from reference concentration are quite high for some of the samples (20–30%) and the deviation is increasing with time for the lean solvents. This is assumed to be affected by HSS and degradation products. The parity plot for MEA and CO₂ (predicted concentrations from the model PLS 10–80%) given in Fig. 18 also illustrate this trend for CO₂.

Also, in this case sample residuals were calculated. A plot of the sample residuals versus time for these samples are shown in Fig. 19. The shown residuals are obtained from the model PLS 10–80%. For both rich and lean there is a nearly linear increase with time which is assumed to be caused by an increase in degradation during the period.

4. Conclusion

The use of PLS-R model based on FTIR spectra is a technique that could be used for online analysis of the main components (MEA, CO₂ and H₂O) of MEA solvent. This work with PLS-R models shows that pre-

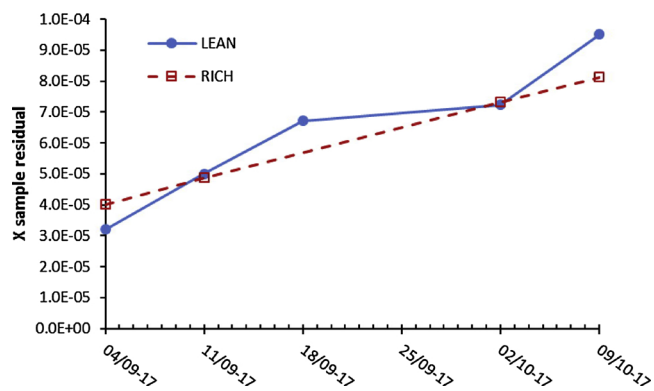


Fig. 19. Calculated X sample residuals for MEA samples from TCM campaign.

treatment of the spectra improves the prediction capabilities of the models. Spectral pre-treatment with square root transformation was shown to give better analytical predictions on realistic solvent samples. Furthermore, the introduction of density in the calibration models makes some improvement.

The effects of the presence of several of major degradation products in MEA solvent on model prediction and robustness was investigated. It was found that for most of the degradation products tested, a calibration and quantification of the degradation products with the FTIR and PLS-R is not possible for the typical concentration range of these products (< 0.5 wt%). Additionally, the effect on the prediction of the solvent compounds (MEA, CO₂ and H₂O) is small for these concentration range of the degradation products. There is however an exception for typical heat stable salt compounds, where we have run samples containing formate and sulphate. Here a significant effect on the spectra was observed as well as on model prediction, when concentration of these salts exceeds around 0.5 wt%.

The sample residuals (i.e. part of the data that are not modelled) contains useful information and in this work we have seen that increase in the residuals is an indication of changes to the solvent (like increased HSS). Thus, the residuals may be an important factor to monitor during solvent test campaigns. Specific monitoring of individual degradation products and contaminates is important. As the sensitivity of the spectroscopic techniques is not as good as for dedicated off line analysis (concentrations may be in the g/l range before degradation products can be quantified) an alternative maybe to monitor residuals and set an alert when significant changes in the solvent appear. When this alert appears dedicated off line analysis could be applied for determination of specific degradation products.

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