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Vacuum assisted acidification: A novel, robust and accurate technique for the measurement of CO_2 loading in solvents and its application in post combustion capture

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Abstract

A method for measuring the CO_2 loading of post combustion capture solvents has been developed which first separates CO_2 from the solvent by acidification of the solvent under vacuum conditions, then traps the CO_2 via deposition, and finally quantifies the CO_2 by pressure measurement in a calibrated volume. A preliminary comparative assessment shows that the measurement accuracy and precision of the method compares favorably to other methods currently used at post combustion capture research facilities and that there is potential for continuing development of the method for use in industrial field applications.

Peer-review under responsibility of the Organizing Committee of GHGT-12

Keywords: CCS, CO_2, Post Combustion, CO_2 loading measurement, Solvent Analysis

1. Background

The accurate determination of CO_2 loading in amine solvents is critically important for post combustion capture (PCC) plant process control, plant optimisation, and economic operation. The ideal CO_2 loading measurement method is required to have several characteristics to be fit for use at PCC industrial scale. First, the method must be sufficiently accurate to enable effective plant optimisation and control. Second, the method must be robust to operate effectively in the field for long periods of time and require minimal maintenance and operator intervention. Third, the method must be versatile and capable of analysing solvents and sorbents over a range of CO_2 loadings

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with a variety of chemistries in addition to maintaining its measurement performance despite the presence of solvent degradation products and heat stable salts. Fourth, the method must have a sufficiently fast measurement time to incorporate into various automated process control loops used during plant operation. Finally, the method should be economical with respect to initial capital cost and the long term operational costs of the equipment.

A family of titration analysis methods has been developed for CO_2 loading measurement. They analyse the CO_2 present in the solvent by the addition of a base to then measure both the pH [1] and the conductivity [2] of the solution. Additional methods dissolve the sample in methanol prior to titration for better accuracy [3]. Other titration methods precipitate the CO_2 from the solution prior to titration analysis [4, 5, 6]. A second family of analysis methods separates the CO_2 from the solution by excess acid addition and quantify the CO_2 by measuring physical gas displacement [7], sweeping the CO_2 through an IR detector [8, 9], or sweeping through a standard caustic solution [10]. A third family of analysis methods based on spectroscopy measures CO_2 loading by identifying and quantifying the CO_2 salt species in-situ by FTIR [11, 12, 13], Raman IR [14, 15], and NMR [16, 17, 18]. While all these methods are effective they may not sufficiently meet the combination of five ideal criteria described previously, which would make them the routine CO_2 loading measurement technique for full-scale post combustion capture applications.

A new method for CO_2 loading measurement of amine solvents is presented here, which separates CO_2 from the solvent sample by the addition of excess acid under vacuum conditions, and then collects the CO_2 via deposition in a gas sample chamber. The method is similar to a calibration standard method used for determining the inorganic carbon concentration in seawater [19, 20]. The recovery of CO_2 is further enhanced by iteratively degassing the solvent under vacuum conditions and the CO_2 quantification is enhanced by measuring the separated CO_2 into a calibrated volume container using a high accuracy pressure transducer rather than a gas displacement manometer.

2. Experimental

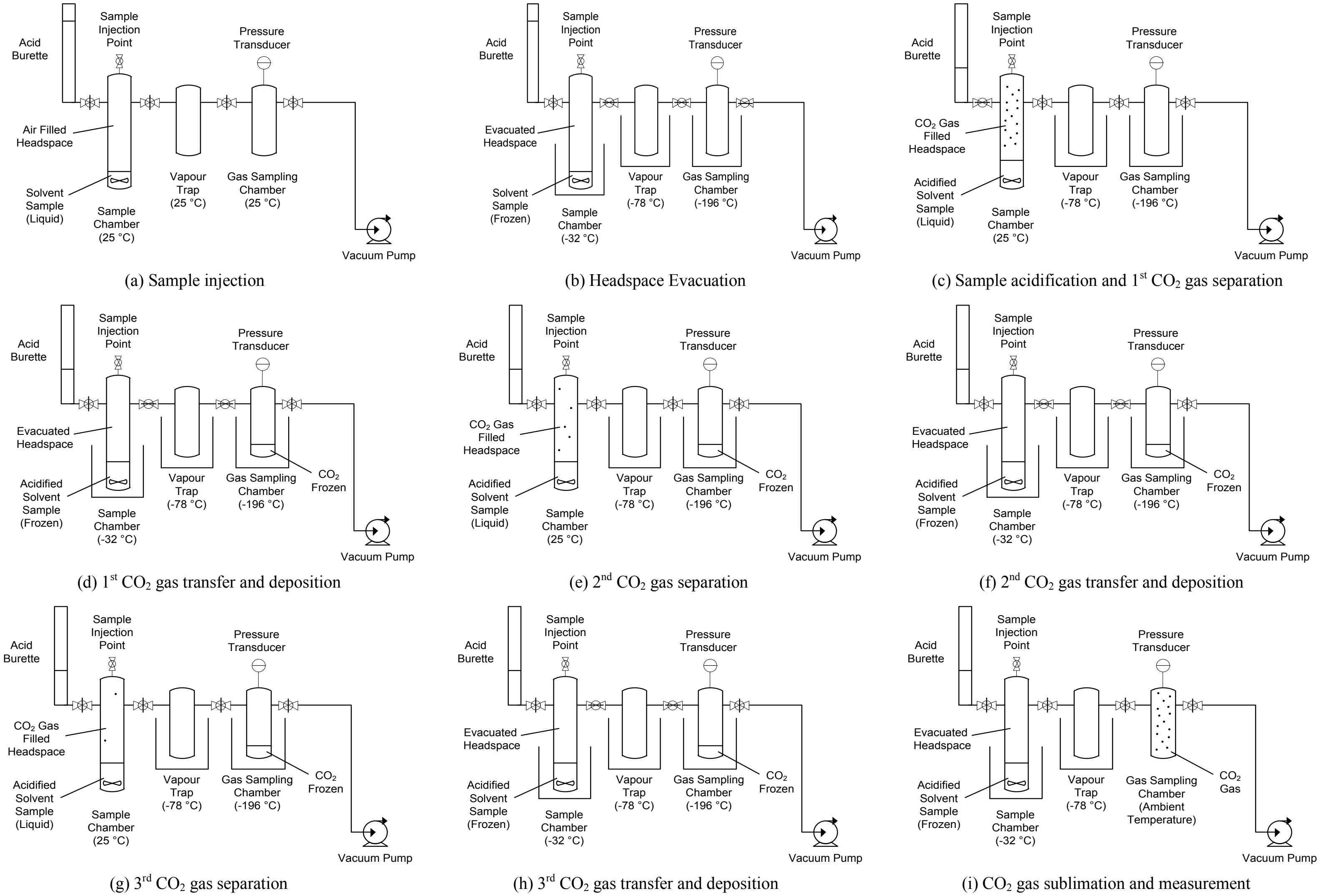
2.1. Experimental Components

The acid burette, sample chamber, vapour trap, gas sampling chamber, and transfer lines were all constructed from borosilicate glass. Threaded Polytetrafluoroethylene (PTFE) tap valves with integrated O-rings are used to isolate each piece of equipment under vacuum conditions. The vacuum pump is manufactured by Edwards Pumps. The pressure transducer is a Baratron capacitance manometer manufactured by MKS Instruments and has a calibrated range of 760.0 Torr with a measurement uncertainty of 0.1 Torr.

2.2. Experimental Set-up and Procedure

A schematic sequential diagram of the method procedure is illustrated in Figure 1. The method begins by injecting a known mass of solvent sample into the sample chamber via pipette (Figure 1a). The sample is frozen to approximately -32°C using a chilled acetone solution in order to prevent water and amine vapour from transferring to the gas sampling chamber. The gas sampling chamber, vapour trap, and sample chamber are then evacuated with the vacuum pump. The gas sampling chamber is then cooled to -196°C with liquid nitrogen and the vapour trap is cooled -78°C with dry ice (Figure 1b). The gas sampling chamber, vapour trap, and sample chamber are isolated from the vacuum pump and from each other and the solvent is allowed to thaw to ambient conditions.

2.4 M HNO_3 aqueous acid is then added in excess to the sample chamber (~5 mol acid / 1 mol amine) from the acid burette to facilitate CO_2 gas separation from the solvent sample into the evacuated sample chamber head space. A Teflon coated magnetic stir bar is used to agitate the sample during CO_2 separation (Figure 1c). After gaseous CO_2 has separated from the solvent sample, the liquid in the bottom of the sample chamber is again frozen to approximately -32°C in order to prevent water and amine vapour from transferring to the gas sampling chamber. The isolation valves between the gas sampling chamber, vapour trap, and sample chamber are then opened. The CO_2 gas separated from the solution passes from the sample chamber head space through the vapour trap to freeze any residual moisture and finally deposits into the gas sampling chamber as a CO_2 solid. Residual gasses that have not deposited in the gas sampling chamber (O_2, N_2, Ar, etc.) are then pumped from the system using the vacuum pump (Figure 1d).



(a) Sample injection

(b) Headspace Evacuation

(c) Sample acidification and 1st CO_2 gas separation

(d) 1st CO_2 gas transfer and deposition

(e) 2nd CO_2 gas separation

(f) 2nd CO_2 gas transfer and deposition

(g) 3rd CO_2 gas separation

(h) 3rd CO_2 gas transfer and deposition

(i) CO_2 gas sublimation and measurement

Figure 1(a)-(i): Process Steps of the Vacuum Assisted Acidification Method for the CO_2 Loading Measurement of Carbon Capture Solvents

The gas sampling chamber, vapour trap, and sample chamber are isolated again from the vacuum pump and from each other. The chilled acetone solution is removed allowing the solvent sample to thaw, promoting further CO_2 gas separation (Figure 1e). The process of freezing the acidified solvent sample, transferring and depositing the separated CO_2 gas and pumping away the non-deposited residual gasses is repeated twice more for a total of three CO_2 gas transfers (Figures 1f - 1h). The gas sampling chamber is isolated from the vapour trap and vacuum pump, the liquid nitrogen coolant is removed from the gas sampling chamber, and the deposited CO_2 solid in the gas sampling chamber is allowed to sublimate as the chamber returns to ambient temperature. The CO_2 gas present is quantified using the ideal gas law by measuring the pressure in the gas sampling chamber with a high accuracy pressure transducer and the ambient temperature using a mercury thermometer (Figure 1i).

3. Determination of Method Accuracy and Precision

In order to determine the method's accuracy and precision, six analytical powder samples of $CaCO_3$ (purity 99.995%) were analysed for CO_2 loading. Each powder sample with masses between 0.214g – 0.323g was dried in a convection oven at 120°C for ~30 minutes to drive off residual moisture then weighed with an analytical balance prior to being added to the sample chamber. The CO_2 loading as measured by the vacuum assisted acidification method was compared to the expected CO_2 loading value. The measurements were also performed in duplicate with identical mass samples to determine the precision of the method (Figure 2).

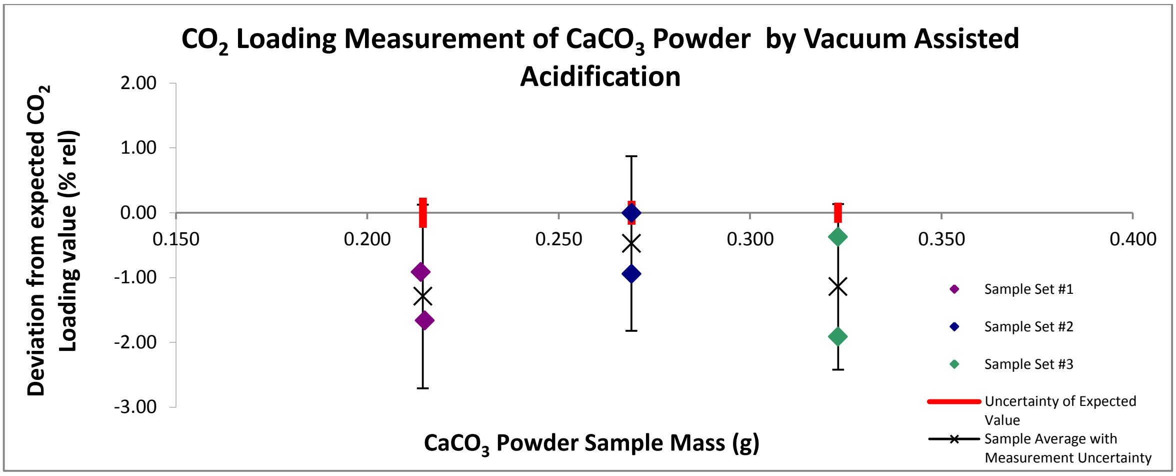


Figure 2: CO_2 loading results of three duplicate sets of $CaCO_3$ powder as measured by the vacuum assisted acidification method. The results are plotted as the % relative deviation from the expected amount of CO_2 present for each $CaCO_3$ powder sample. The % relative uncertainty (0.310% - 0.467%) in the amount of CO_2 present is calculated from sample mass uncertainty (+/- 0.001 g) and sample purity uncertainty (+/- 0.005% purity) and shown with a solid bar on the x-axis for each sample set. The average result of the sample sets is also plotted with error bars corresponding to the method's measurement uncertainty calculated using an error propagation calculation.

The vacuum assisted acidification method shows an average measurement accuracy of 0.971% relative to the expected value when measuring the analytical standard $CaCO_3$ powder with the maximum measurement deviation being 1.96% relative to the expected value and the minimum measurement deviation being 0.006% relative to the expected value. The average measurement uncertainty of the method was determined to be 1.34% relative to the expected value using a compounding error calculation. The method demonstrated reasonable repeatability with the duplicate pairs deviating from each other on average by 0.932% relative to the expected value and all six measurements falling within the measurement uncertainty range. The initial accuracy and precision results for analytical CaCO3 powder samples demonstrated the potential for a highly accurate and precise method compared to current techniques and a second study was performed on a more realistic loaded MEA solution.

4. Comparison to industry standard CO_2 loading measurement methods – An MEA solvent analysis example

4.1. Laboratory Based CO_2 Loading Procedure of MEA solvent

In order to demonstrate the accuracy and precision of the vacuum assisted acidification method in an applied PCC context, a laboratory made CO_2 loaded solvent sample was created using a new method, which minimises CO_2 transfer between the solvent and the ambient atmosphere prior to analysis (Figure 3). A 30.00 wt% MEA (uncertainty: +/- 0.16 wt% MEA) solution was prepared by weight using neat MEA (purity 99%) and degassed deionised water on an analytical balance. A sample of this unloaded solvent with a known mass was injected via septum into a glass bulb with a known mass of pure CO_2 gas. The unloaded MEA solvent was allowed to absorb the CO_2 inside the sample vessel achieving a CO_2 loading of 0.4639 mol CO_2 / mol MEA (uncertainty: +/- 0.0048 mol CO_2 / mol MEA). As the water was thoroughly degassed prior to use and the neat MEA chemical was kept with care in a sealed container prior to use, the residual CO_2 in the unloaded solvent sample prior to injection is presumed to be negligible. Based on previously published equilibrium equations [21] and previous equilibrium studies [22] it is assumed that the CO_2 partial pressure of this loaded MEA solution at 25°C is negligible and therefore all CO_2 present is assumed to absorb into the solution.

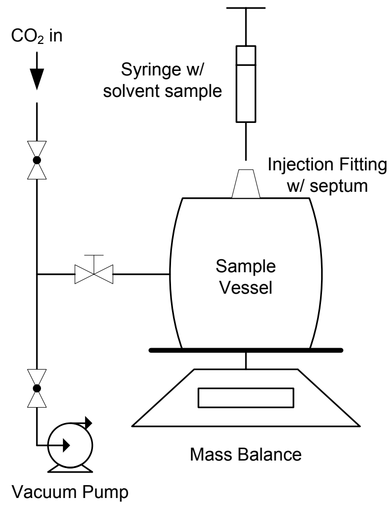


Figure 3: A schematic of a method for the CO_2 loading of a solvent sample. The method first evacuates a sample vessel with a vacuum pump, tares the vessel, then fills the vessel with pure CO_2 gas and measures the mass of CO_2 on a mass balance. A solvent sample of a known mass is injected into the sample vessel via syringe and allowed to absorb the CO_2 gas in the vessel and cool to room temperature prior to removal and analysis. The method significantly reduces possible occurrence of CO_2 transfer between the solvent and the ambient atmosphere.

4.2. Comparison to Industry Standard CO_2 Loading Measurement Methods

The CO_2 loading of the MEA solvent solution was measured by vacuum assisted acid separation in duplicate and compared to the expected CO_2 loading value (Figure 4). For comparison, the accuracy and precision results of 3 other industry standard CO_2 loading measurement methods used at industrial research facilities [23, 24]. These methods were used to analyse similar lab made MEA solvents loaded with CO_2 from a 30wt% MEA stock. The method used to load CO_2 into these solutions [9] differs slightly from the method outlined in this work and the specific CO_2 loadings of the MEA solutions analysed were 0.2530 mol CO_2 / mol MEA for end point titration, 0.5200 mol CO_2 / mol MEA for the inorganic carbon, 0.4586 mol CO_2 / mol MEA for Chittick gas displacement.

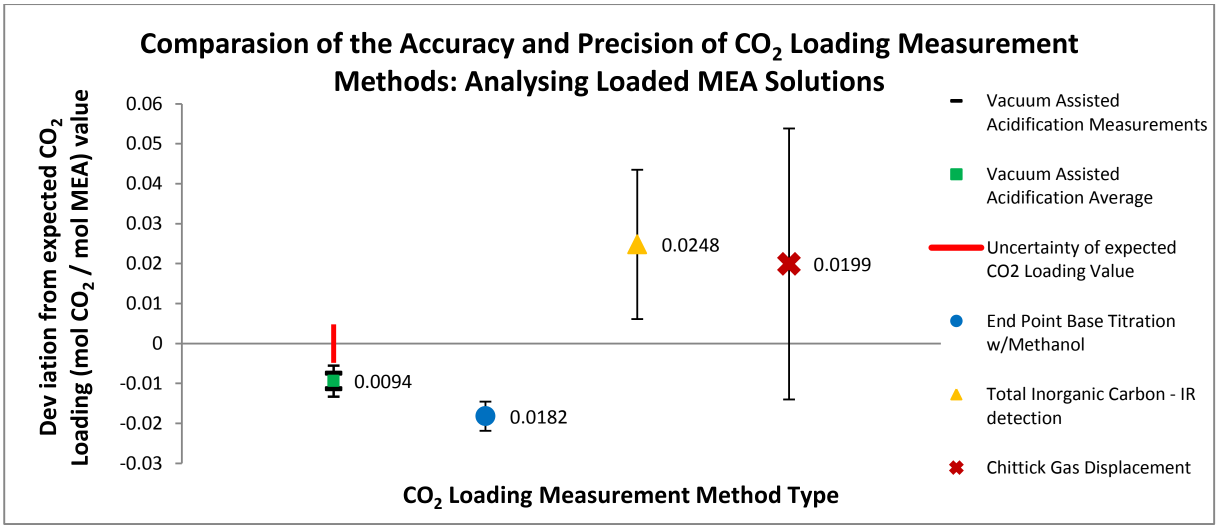


Figure 4: A comparison of measurement accuracy and precision for the vacuum assisted acidification method and three other industry standard CO_2 loading measurement methods used in the field at industrial PCC research facilities [23, 24]. The average deviation from the expected CO_2 loading value (mol CO_2 / mol MEA) for laboratory made loaded MEA solvents is plotted for each measurement method. For the vacuum assisted acidification method, the CO_2 loading uncertainty of the lab made sample is plotted on the x-axis with a solid bar. This information was not available for the other measurement methods. The error bars represent the spread of repeated measurements and give an indication of the precision of the methods.

The vacuum assisted acidification procedure shows an average measurement accuracy of 0.0094 mol CO_2 / mol MEA relative to the expected value of 0.4639 mol CO_2 / mol MEA when measuring the loaded MEA solvent solution. The maximum measurement deviation is 0.0114 mol CO_2 / mol MEA relative to the expected value and the minimum measurement deviation is 0.0077 mol CO_2 / mol MEA relative to the expected value. The average measurement uncertainty of the method was determined to be +/- 0.0048 mol CO_2 / mol MEA relative to the expected value again using a compounding error calculation. The method again demonstrated reasonable repeatability with the duplicate pair deviating from each other by 0.0037 mol CO_2 / mol MEA relative to the expected value and again fell within the measurement uncertainty range.

The vacuum assisted acidification method appears to demonstrate superior accuracy and precision in practice compared to the Chittick gas displacement method [25] and the total inorganic carbon analysis methods [8]. It also appears to demonstrate similar or slightly superior accuracy and precision compared to the high precision auto-titration based technique [3]. The vacuum assisted acidification method also may have a competitive advantage compared to the titration based technique by design, as it should not suffer significant performance losses observed with titration based methods when analysing complex blended solvents contaminated with inorganic cations and weak acid anions which form heat stable salts [26].

5. Conclusions

The superior measurement accuracy and precision, the ability to measure loadings of complex contaminated solvents, and the potential for process optimisation and automation suggests that the vacuum assisted acidification CO_2 loading measurement method may be able to provide the accuracy, robustness, versatility, speed, and low cost required for use in industrial PCC applications. Future work will focus on determining the method's performance on complex pilot plant samples compared to state-of-the-art methods. Parametric studies will then be conducted to increase measurement accuracy and reduce method complexity and measurement time.

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