

## ACT LAUNCH Project No 299662



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Lowering **A**bsorption process **U**ncertainty, risks  
and **C**osts by predicting and controlling amine  
degradation

### Deliverable Nr. D.3.3.3

**A document describing the evaluation of the two methods used to measure volatility of degradation compounds Memo describing the results of the volatility of degraded solvents using the simple boiling method**

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Written By	Vanja Buvik (SINTEF) and Hanna K. Knuutila (NTNU)	Date: 29.03.2023
Checked by	Andreas Grimstvedt (SINTEF)	Date: 29.03.2023
Approved by the coordinator	Peter van Os (TNO)	Date: 06.04.2023
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# 1 Introduction

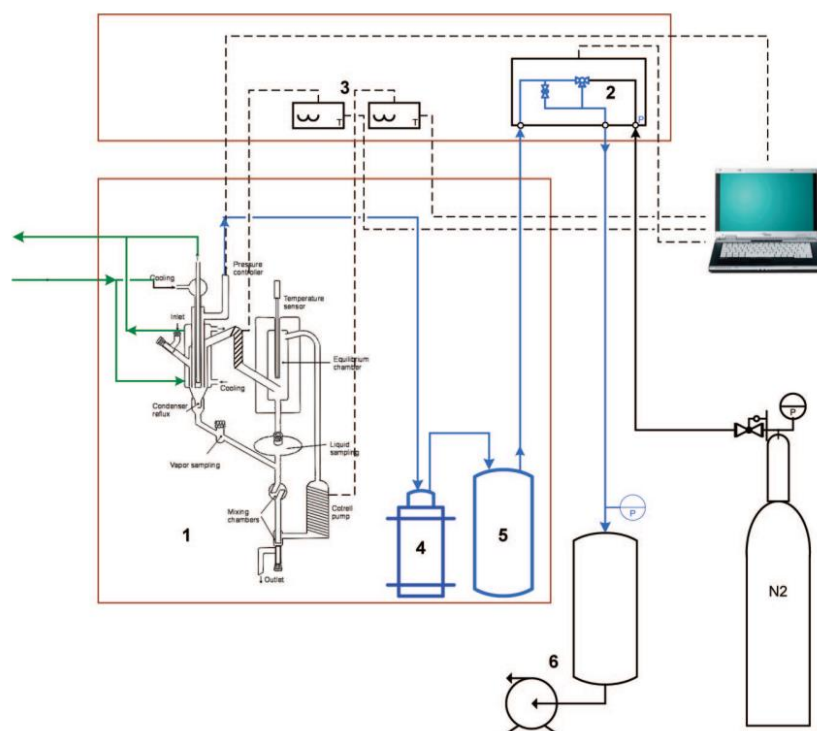
This document gives a brief description of the two different methods used in the reports D.3.3.1 and D.3.3.2 and compares the results and applications of these in assessing potential emissions for amine solvents for CO<sub>2</sub> capture. One of the challenges of amine scrubbing for CO<sub>2</sub>-removal from post-combustion flue gases, is that the process may cause emissions of other compounds if a rigorous mitigation system is not in place. These emissions may consist of the amine components which are performing the chemical absorption of CO<sub>2</sub> themselves, or their degradation products. Since emission control is of such high environmental importance, it is beneficial to be able to assess this in an early stage of solvent development. A method for identifying the volatility of the solvent and its degradation products is, therefore, necessary to qualify a new solvent. These two methods were tested in LAUNCH WP3.3 for the purpose of finding a fast way to assess the potential emissions of various amine solvents.

## 2 Experimental methods

### 2.1 Ebulliometer

The Świątosławski ebulliometer can measure boiling points of solvents by measuring the temperature of the vapor–liquid equilibrium. A schematic of the ebulliometer is thoroughly presented in I. Kim et al. 2008<sup>1</sup> and a schematic is shown in Figure 1. It provides a rapid methodology for measuring pressure, temperature and the composition of both liquid and condensate phases, which in turn is used for determining the vapour–liquid equilibria of the solution. About 100 mL of the solution is introduced into the liquid sample chamber, before the system is sealed and the pressure can be reduced and controlled. The heaters allow for temperature adjustment, to the desired temperature, which in this case was around 50–100 °C. the liquid sample is partially evaporated in the Cottrell pump, and the sample is drawn into the equilibrium chamber, where a vapour–liquid equilibrium is established by condensing the liquid and the gas phase doing to the condenser. When no changes in the pressure or temperature are observed for 30 minutes, it is assumed that the system has reached equilibrium, and sampling is performed from the liquid phase, using a syringe. A sample is also taken from the condensate in the vapour sampling port, if there is a sufficient liquid build-up for a sample.

A thorough description of the method used for these experiments can be found in D3.3.1.

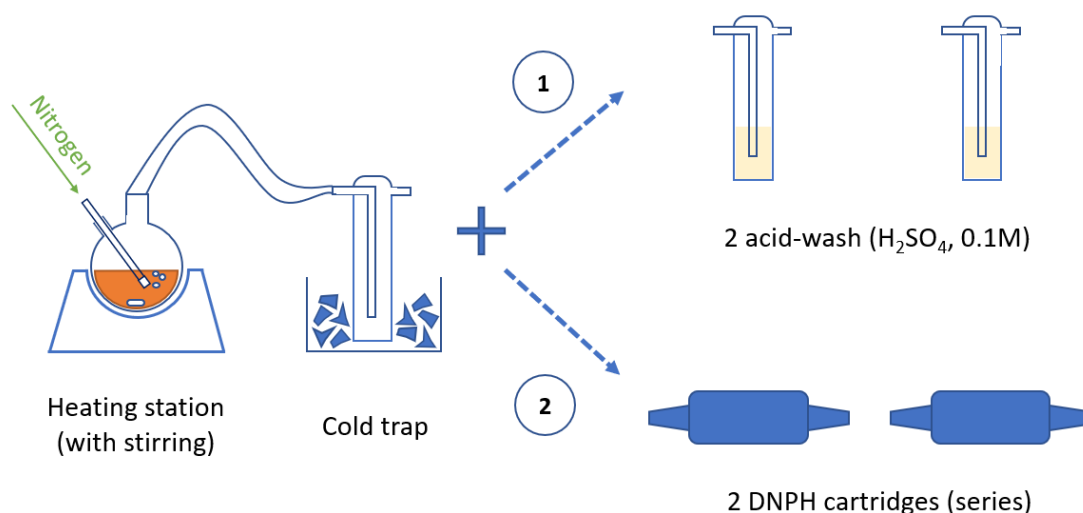


**Figure 1: Schematic of the ebulliometer setup used for this methodology, reprinted from I. Kim et al 2008.<sup>1</sup> 1: ebulliometer; 2: pressure controller; 3: heaters control; 4: cold trap; 5: buffer vessel; 6: vacuum pump with a buffer vessel**

<sup>1</sup> I. Kim, H. F. Svendsen, and E. Børresen. “Ebulliometric Determination of Vapor–Liquid Equilibria for Pure Water, Monoethanolamine, N-methyldiethanolamine, 3-(Methylamino)-propylamine, and Their Binary and Ternary Solutions”. Chem. Eng. Data 2008, 53, 11, 2521–2531, <https://doi.org/10.1021/je800290k>

## 2.2 Simple boiling method

The simple boiling method, as depicted in Figure 2, consists of a round bottom three-neck glass flask containing 200 mL of the studied solution on an electric heating mantle. N<sub>2</sub> gas is sparged in through one of the side necks of the bottle (100 mL/min) and the central neck of the flask lets the gas phase out of the heated flask into a cold trap, and then either into a series of two acid washes of 100 mL each, or through two 2,4-dinitrophenylhydrazine (DNPH) cartridges. Temperature is measured through the third neck of the flask, tightly fitted with a thermometer. A more thorough description of the method used for these experiments can be found in D3.3.2.



**Figure 2: Schematic of the simple boiling method.**

The experiments were conducted by sparging gas through the amine solutions at 80-90 °C for 2.5 hours. Samples were collected from the start solution, condensate, acid washes, and compounds were extracted from the DNPH cartridges and analysed.

## 2.3 Analytical procedures

The analyses of the samples were the same for the two experimental procedures, apart from the extraction of compounds from the DNPH cartridges, which was only done from the simple boiling method. The cartridges were extracted with a procedure developed at SINTEF Biotechnology and the content was analysed by LC-MS.

### 2.3.1 CO<sub>2</sub> quantification using total inorganic carbon analysis

The CO<sub>2</sub> concentration or "CO<sub>2</sub> loading" of the amine (mol CO<sub>2</sub> per mol alkalinity/amine) was determined using a Total Organic Carbon (TOC) analysed from Shimadzu in total inorganic carbon mode. For this method, the sample is diluted to contain < 500 ppm inorganic carbon and is then added to 25wt% H<sub>3</sub>PO<sub>4</sub> (aq.), where the acidification and sparging with synthetic (CO<sub>2</sub> free) air releases all inorganic carbon, such as that bound in carbonates, bicarbonates, and carbamates, as CO<sub>2</sub>. CO<sub>2</sub> can then be detected in a non-dispersive infrared

detection (NDIR) cell. The quantification of CO<sub>2</sub> is then done by back-calculation and calibration with NaHCO<sub>3</sub>, using the relative intensity of the NDIR signal. The typical uncertainty of this method is  $\pm 2\%$ .<sup>2</sup>

### **2.3.2 Liquid chromatography coupled with mass spectrometry (LC-MS)**

All single species, except CO<sub>2</sub>, were quantified using liquid chromatographic separation followed by a triple quadrupole MS, where molecular ions are selected in the first quadrupole, the second is used as a collision cell and the third quantifies the compounds based on selected fragments of the initial molecule ion (QqQ configuration). This approach makes it possible to identify and quantify compounds with high certainty and accuracy. The instrument used was an UHPLC Agilent 1290 Infinity System with an Agilent 6490 Triple Quadrupole detector.

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<sup>2</sup> Buvik, Vanja, et al. "Stability of structurally varied aqueous amines for CO<sub>2</sub> capture." *Industrial & Engineering Chemistry Research* 60.15 (2021): 5627-5638.

### 3 Comparison of the two tested methods

The two methods are both for determination of volatility of solvent mixtures, and to determine which compounds will evaporate from the blend. The simple boiling method is, as the name already indicates, quite simple. The apparatus is easy to build and does not require very advanced parts, compared to the ebulliometer. On the other hand, as the ebulliometer provides vapor-liquid equilibrium data, it consists of accurate pressure and temperature measurements and special design reactors. It also requires trained personnel to operate and will be more costly and time-consuming to build than the equipment for the simple boiling method.

The ebulliometer provides vapor-liquid equilibrium (VLE) data for both degraded and non-degraded solutions and concentrations relevant to water wash and the circulating solvent. This means that the data can be used to fit, for example, the VLE models used in water wash sections. Ebulliometer can also be used to map VLE behaviour of a system over a large range of conditions (amine concentrations), making it suitable for providing data needed for aerosol models also. The simple boiling method on the other hand, aims only to identify volatile degradation compounds qualitatively, and cannot produce data suitable for fitting thermodynamic models.

Experimental results from the LAUNCH project show, that both methods find volatile components, and the most volatile components of degraded amine solutions (amine itself and ammonia) were qualitatively identified with both methods. While the ebulliometer can be used to measure equilibrium, the short-cut method can only be used to identify volatile components.

Common for both methods is that they rely on a robust and thorough understanding of the composition of the solutions to be measured. Here, LC-MS is used to identify and quantify known degradation compounds, as well as the original amines in the gas phase and liquid samples. Without knowledge of the solvent composition, meaning what degradation compounds it contains, one simply cannot know what to look for in the acid wash, condensate, or cartridges. The LC-MS analysis, combined with the knowledge of what degradation compounds to expect from a given amine, adds to the complexity of both methods, making even the simple boiling method impossible if the degradation components of the solvent in question are not known. Therefore, the main drawback for both methods is the requirement that the degradation compounds of the amine solvent are already known, and analytical methods are developed. This is the most demanding part of the work. After the degradation compounds are known (and some degraded solution is available), the ebulliometer type of experiments can be used to study the volatility of the degradation compounds. Alternatively, a short-cut method type of experiments could be used to identify potential components to be monitored in emissions and studies during piloting.

If the composition of the solution is known and analytical methods are in place that can quantify the components in the acid wash or DNPH cartridges for the simple boiling method, or in the condensate for the ebulliometric method, both experimental approaches will identify the most volatile components of the mixture. The advantage of the ebulliometer over the simple boiling method, is that it can produce quantitative data that can be used i.e., for modelling purposes. If what you need is just to know which components of a mixture are the most volatile, the simple boiling method can also give sufficient insight.