Ref. Ares(2025)1625949 - 28/02/2025

TheHorizon Europe (HORIZON)
Marie Skłodowska-Curie Actions
Doctoral Networks (MSCA-DN)

MISSION-CCS: Material Science Innovation for Accelerated, Sustainable and Safe Implementation of Carbon Capture and Storage

Deliverable D2.1 – Guideline on optimum tools/techniques for solvent degradation/corrosion characterization

Month Due: M13

Month Delivered: M13

Project Co-ordinator Name	Dr Wei Yan
Project Co-ordinator Organisation Name	DTU
Report Prepared by	**Georgios Oikonomou (NTNU)** **Prof. Hanna K. Knuutila (NTNU)** **Dr. Vanja Buvik (SINTEF)**

Dissemination Level of Report

PU	Public	**x**
SEN-PP	Restricted to program participants and Commission Services	
SEN-RE	Restricted to a group specified by the consortium (including the Commission Services)	
SEN-CO	Confidential, only for members of the consortium (including Commission Services)	

Reviews and Approval:

Version	**Date**	**Comment**	**Modifications made by**
D2.1	20/02/2025	First Draft	Created/edited **Oikonomou, Buvik and Knuutila**
	27/02/2025	Review	
		Sign-off as Supervisory Board	

Executive Summary

This report aims to highlight important techniques and analytical methods used for the characterization of degradation and corrosion in amine solvents utilized for CO_2 capture. The introduction provides a brief overview of the CO_2 capture process via chemical absorption, including basic information about the solvents used and the main challenges related to degradation and corrosion. It then lists the primary compounds of interest in degradation and corrosion studies, along with their specific characteristics and the often used chemical analysis methods for monitoring them. Each method is shortly described, focusing on its fundamental aspects, limitations and specific applications related to CO_2 capture. Finally, some key aspects of the described methods are summarized in the conclusions, and additional publications are recommended for further information on degradation monitoring analysis.

1. Introduction

MISSION-CCS is a Marie Skłodowska-Curie Actions Doctoral Network (MSCA-DN) program that provides training to 13 Doctoral Candidate Researchers (DCRs), focusing on the mitigation of degradation phenomena across the entire CCS chain. The interdisciplinary network includes 4 academic institutions (DTU, Univ. of Leeds, NTNU, INSA Lyon) and 12 other associated members across 7 countries, who are at the scientific forefront of combining material science, engineering, physics, chemistry and techno-economics to develop the next generation of research and innovation leaders in the field of CCS.

1.1. CO_2 capture via chemical absorption

Of the various methods to separate CO_2 from industrial gases, post-combustion, absorption-based CO_2 capture, using aqueous alkanolamine solutions is the most mature due to its high processing capacity, excellent adaptability, and reliability [1]. The CO_2 absorption process takes place in an absorption column filled with packing material, where the industrial flue gas is brought into contact with the absorbent (solvent). The bonding reactions between CO_2 and the amine are highly exothermic and the absorption column typically operates around 40-70°C. Once the CO_2 has been absorbed, the solvent is transferred to a stripper column, where it is heated by a reboiler, so that the captured CO_2 is released. The stripper usually operates around 2 bar and at temperatures between 100-140°C. The regenerated lean solvent is then recycled back to the absorption column. The captured CO_2 recovered at the top of the stripper can be compressed and stored, or utilized for various applications, such as enhanced oil recovery or the production of valuable chemicals.

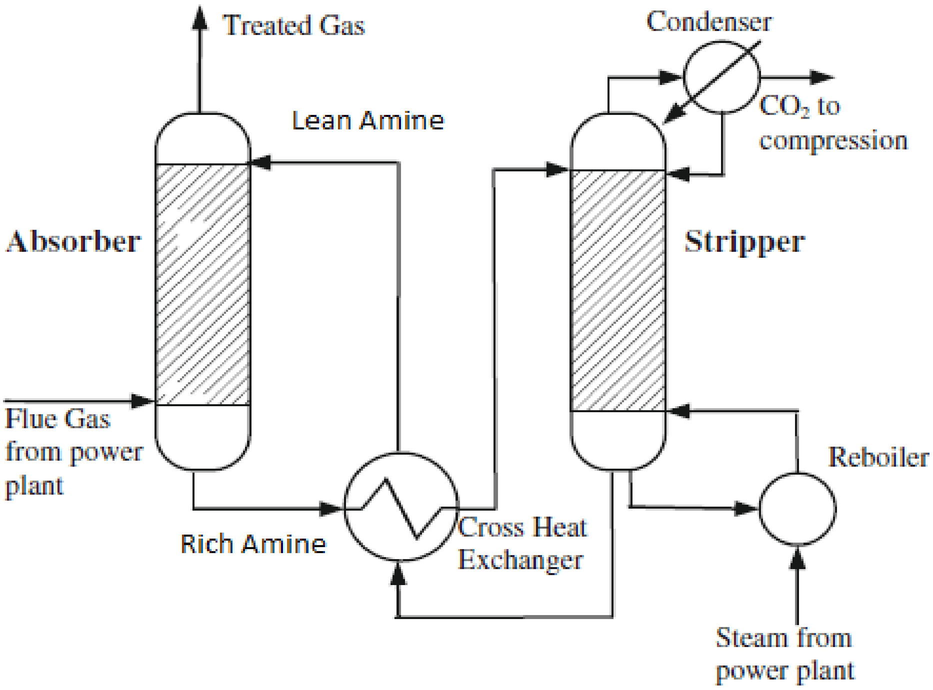
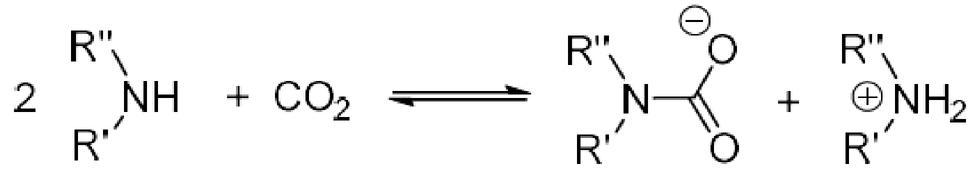
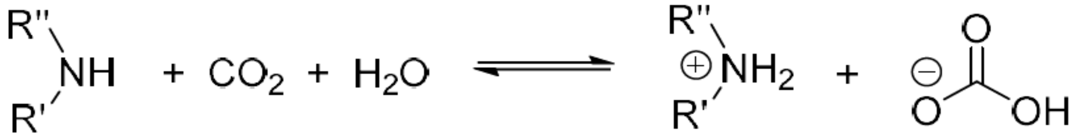


Figure 1: Simplified process flow diagram of chemical absorption process for post combustion CO_2 capture [2].

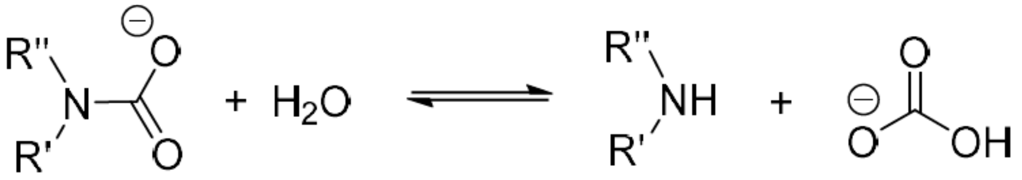
A variety of amines can be utilized as absorbents and typically they are introduced to the absorption process as aqueous solutions (e.g. 30% wt. MEA). Ethanolamine (MEA) has long been considered the benchmark solvent due to its fast absorption rate, low volatility and low price [3], while diethanolamine (DEA), methyldiethanolamine (MDEA), piperazine (PZ) and 2-amino-2-methylpropanol (AMP) are also effectively utilized in CO_2 capture. Furthermore, different amine blends have been investigated as capable solvents and study results have indicated that a particular blend of PZ and AMP (CESAR1) could suggest a new benchmark solvent [4]. For primary and secondary amines, the reversible binding of CO_2, takes place through 3 reaction mechanisms: carbamate formation (Eq. 1), bicarbonate formation (Eq. 2), and carbamate reversion (Eq. 3). Tertiary amines primarily bind CO_2 through bicarbonate formation (Eq. 4). Primary and secondary amines typically absorb CO_2 faster than tertiary amines, which react slower but normally have higher theoretical absorption capacities. The reversal of CO_2 binding reactions' equilibria during the desorption phase requires a significant heating duty, which leads to relatively high operating costs [5].



Eq. 1



Eq. 2



Eq. 3

Eq. 4

Degradation is the irreversible transformation of an absorbent solution into other compounds. Amine degradation can be oxidative or thermal. Oxidative degradation is attributed to the presence of dissolved oxidizing agents in the flue gas (i.e., O_2, and NO_X) and primarily takes place in the absorber. Thermal degradation takes place in the desorption column (stripper) due to heat and CO_2 presence [6]. The formation of degradation products in the system is slow, but over time leads to problems such as amine loss, fouling, foaming and reduction of CO_2 absorption capacity [7]. Degradation products also promote equipment corrosion which, over time, can reduce the efficiency of the process and cause unscheduled downtime. Furthermore, dissolved metals act as catalysts towards degradation reactions and therefore corrosion often increases degradation. Although degradation and corrosion have been studied extensively, further theoretical and experimental research is needed to fully understand their effects on CO_2 capture and develop efficient methods to minimize these impacts.

2. Analytical methods available to monitor solvent degradation and corrosivity

The variety of degradation products and the fact that they are often present in very small concentrations, as well as the dynamic correlation between degradation and corrosion, make experimental monitoring of amine ageing rather challenging. Furthermore, degradation products can be volatile, toxic, thermally unstable etc. Different analysis methods need to be employed, depending on the properties of the targeted compounds. Table 1 lists typical compounds of interest. Amine concentration and CO_2 content of the solvent are important to monitor to ensure good daily process operation. The table also provides the most common classes of degradation compounds to be monitored, the main challenges related to these compounds, and the analytical methods used to monitor them. The different analysis methods will be shortly discussed next.

Table 1: Compounds of interest in absorption-based CO_2 capture and suggested analysis techniques

Compound	Characteristic	Analysis
Ammonia	Volatile, toxic	LC-MS with derivatisation or FTIR
Amides and other degradation products	Varying characteristics	LC-MS
Nitrosamines and nitramines	Carcinogenic, often volatile	GC-NCD
Volatile organic compounds	Volatile, often toxic	GC/LC-MS
Heat stable salts (HSS)-Organic acids/carboxylates	Ionic compounds	Ion exchange followed by titration or, ion chromatography (IC), HLPC-UV, LCMS with derivatisation
Dissolved metals	Form complexes in solution	ICP
Amines (solvent)	Degradable when loaded with CO_2	LC-MS and titration
Carbon dioxide	Bonds with amines	Inorganic carbon analysis (i.e., on a TOC analyser)

2.1. Titration

Titration is a well-established quantitative analytical technique used to determine the unknown concentration of a specific substance (analyte). It is performed by gradually adding a specific reagent (titrant) of known concentration, which reacts with the analyte in a definite proportion, to the sample to be analysed. The titrant is added until the chemical reaction is completed, and the end of the titration reaction is usually detected by colour change of a suitable indicator, potentiometry or other techniques (e.g. pH measurement). The measurement of the total titrant volume that was used, allows the calculation of the analyte content based on the stoichiometry of the chemical reaction. Colour change indicators are typically used during manual titration to visually signal the endpoint of the reaction. The selection of the indicator depends on the reaction type, as well as the titrant and analyte. Potentiometry is usually utilized by automated titrators in order to determine the equivalence point of the reaction, which is the point where the titrant and the analyte are present in chemically equivalent quantities. For instance, the equivalence point in an acid-base titration is reached when the moles of the acid neutralize the moles of the base, according to the corresponding chemical equation (without implying that the molar ratio is necessarily 1:1). The equivalence point is determined by measuring the potential difference between two electrodes: One indicator electrode that changes potential based on the ions in the sample, and a reference electrode whose potential is constant. As the titrant is added, the "electrochemical cell" potential is monitored and plotted against the volume of the titrant. The equivalence point is then identified as the steepest point of the curve. Titration is very commonly used in absorption-based CO_2 capture research, to analyse the alkalinity in the CO_2 loaded (and degraded) solvent solutions. Total alkalinity is a measurement of the total concentration of base in a solution. Amines such as ethanolamine (MEA) are weak bases, and the total alkalinity of aqueous amine solvents can be determined by titrating with an acid (e.g. sulfuric acid). However, it is important to consider that some amine degradation products may also be alkaline. Therefore, the total alkalinity measurement of a degraded amine solution, does not necessarily reflect the actual solvent amine concentration, as it is influenced by both the initial amine used, and any alkaline degradation products that may be present [5]. Titration can also be utilized to measure CO_2 and heat stable salts (HSS) presence by using a base titrant instead of an acid, however both cases require pretreatment of the solution. To measure the CO_2 loading, the CO_2 must first be extracted with $BaCl_2$ and then titrated with NaOH, while for HSS measurements, the solution must be treated in a cation exchange resin before titrating with a strong base [5, 8].

2.2. Liquid Chromatography coupled with Mass Spectrometry (LC-MS)

LC-MS is an analytical chemistry technique used for high-precision measurements of multicomponent samples. It combines the physical separation capabilities of high-performance liquid chromatography (HPLC) and the mass analysis capabilities of mass spectrometry (MS). During liquid chromatography, the samples are injected into a flowing solvent stream called the mobile phase. The mobile phase is continuously pumped through a stainless-steel tube (LC column), which contains a specific solid material referred to as the stationary phase. Depending on their properties, the sample components in the mobile phase interact differently with the stationary phase and separate from each other. The components that have the least interaction with the stationary phase emerge from the column first, while all the rest are sequentially flushed out, with the strongest interacting ones emerging last. The time each component spends in the column is called retention time (RT). During chromatography, the mobile phase flowing out of the column (eluent) passes through a detector that responds to a certain property of the analytes. The response measured over time corresponds to the RT of each analyte, which can then be identified by comparing its RT to that of a known compound. This technique, however, is not sufficiently accurate and therefore LC is often coupled with other analysis methods, such as MS. In LC-MS, heat is applied to the mobile phase after exiting the column so that the solvent is evaporated, and the component molecules are vaporized and ionized. Inside the mass spectrometer, the ions are subjected to magnetic fields that separate them from each other, and then measured based on their mass to charge (m/z) ratio [9]. The ion measurements are plotted in a Total Ion Chromatogram. This plot displays the peak intensities of the analyte against their RT, but also a mass spectrum, which depicts the ion abundances versus the measured m/z ratios. LC-MS is often employed during degradation monitoring as it can analyse a variety of degradation compounds such as amine derivatives, nitrosamines, amides and acids. The analysis can be both qualitative and quantitative, but it should be noted that accurate quantification requires calibration with the internal standards of the targeted compounds. Using two-dimensional MS, where the quantification criteria are based on both RT, m/z, and molecule ion fragmentation patterns gives a high analytical accuracy. LC-MS can also be used to identify unknown degradation compounds, however, this is a more challenging task, relying on theoretical predictions that can be difficult to validate [5]. Despite the fact that LC-MS is a very useful and precise analytical method, the relatively high purchase and maintenance cost of the equipment as well as the requirement of a skilled technician to run it, often present obstacles.

2.3. Ion Chromatography (IC)

Ion Chromatography, also known as ion-exchange chromatography, is a form of chromatography in which the separation occurs due to the different coulombic attraction of ions and ionizable polar molecules to an ion exchanger. There are two types of IC: anion and cation exchange. In anion exchange chromatography, negatively charged molecules are loaded and attracted to a positively charged stationary phase, while in cation exchange, positively charged molecules are attracted to a negatively charged stationary phase. Many degradation compounds are known to have ionic properties and therefore IC is often used to study amine degradation. More specifically, anion exchange is used to analyse nitrate, nitrite and carboxylates [10], but it can also be used to determine total amide content, by initially converting the amides to carboxylic acids through hydrolysis [11]. Cation exchange is used for quantitative analysis of amine solvents and Heat Stable Salts (HSS) [5]. In general, IC is cheaper in comparison to LC-MS, however it can only analyse ionic compounds.

2.4. Gas Chromatography coupled with Mass Spectrometry (GC-MS)

In GC-MS, gas chromatography is coupled with mass spectrometry. This method works similarly to LC-MS, with the difference that in GC, the sample is injected into a gaseous mobile phase, for which an inert or unreactive gas is typically selected (e.g. helium, argon, nitrogen). The stationary phase in the GC column can either be an immobilised solid, or a liquid film. This method can be used for quantitative analysis of compounds that vaporize below 300^{o}C. In addition, the analytes must be thermally stable up to 300-500^{o}C, which prevents accurate monitoring of some amine degradation products. Despite this, GC-MS can still be effectively utilized for quantitative measurements and identification of certain degradation compounds [10].

2.5. Gas Chromatography-Nitrogen Chemiluminescence Detector (GC-NCD)

Gas chromatography can also be coupled with a Nitrogen Chemiluminescence Detector (GC-NCD) to detect and quantify nitrosamines. In this technique, the GC eluent enters a quartz tube inside a stainless-steel burner. There it comes into contact with hydrogen and oxygen plasma, that converts all nitrogen compounds to nitric oxide at very high temperatures. Subsequently, the nitric oxide reacts with ozone emitting a proportional amount of light in the red and infrared region of the spectrum. NCD detectors can be adjusted to respond proportionally, only to the presence of thermally unstable nitroso molecule parts, for quantitative analysis of nitrosamines [12]. Nitrosamines are known carcinogens and monitoring them is particularly important when studying secondary amine solvents, which readily form stable nitrosamines in contact with NO_2.

2.6. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

ICP-MS is a type of mass spectrometry analysis method, during which the molecules of a sample are ionized by passing through an inductively coupled plasma (ICP). This plasma is created by inductively heating a gas (such as argon) with an electromagnetic coil so that it is ionized until it becomes electrically conductive. For liquid sample analysis, which is the most common, the sample is first introduced to a nebulizer, which converts the liquid to an aerosol before transporting it to the plasma. Solid samples can also be introduced using different techniques (e.g. laser ablation, electrothermal vaporization), while gas samples can be directly injected into the plasma [13]. ICP-MS is a widely used elemental analysis method capable of detecting element traces at concentrations from 0.1 ppt up to 1000 ppm [14]. In absorption-based CO_2 capture field, it is used to study the corrosivity of different amine solvents by monitoring the accumulated amounts of dissolved metals in the solution [5]. The ICP-MS must be calibrated with pure analytical standards, and analysis is often also done with the addition of an internal standard into the diluted sample.

2.7. Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is an analysis technique based on the molecular vibrations caused by exposure to infrared radiation. In this method a broad spectrum of infrared light is directed through a sample which absorbs part of it, while the rest is collected by a detector that measures the light’s intensity, at different wavelengths. The measured data is then processed to produce a spectrum that reveals the molecular composition of the sample. FT-IR is often used as an online analytical method to monitor gas effluents such as SO_x, NO_x, and CO_2 [5], but also to quantify amine solvent loss and loss of ammonia in the gas released from the absorber [15]. Liquid samples can also be analysed and FTIR can be coupled with a specific sampling technique called Attenuated Total Reflectance (ATR) to monitor the loading and amine concentration in a solvent loop. Theoretically, FT-IR can also be utilized for degradation compound analysis; however, in practice, this is not always possible since these compounds are often present in very low concentrations that are below the detection limit. Moreover, even when the degradation compounds are found in sufficient concentrations, quantification can be challenging since they change the spectra and calibration with degraded solvent is required to ensure accurate results over time.

2.8. Total Organic Carbon (TOC) analyser

The TOC analyser is used to measure the amount of carbon present in a water solution. The total amount of carbon is referred to as "total carbon" (TC) and can be further divided into two categories, total organic carbon (TOC) and total inorganic carbon (TIC). The first step of the analysis is acidification, during which acid is added to the sample so that its pH drops below 3, at which point all carbonate and bicarbonate ions are converted to CO_2. This dissolved CO_2 is extracted (using CO_2-free air) and measured, in order to determine the IC in the sample, which is corresponding to its CO_2 loading. The next step is catalytic combustion at high temperature (>650^{o}C), until all carbon is oxidized to CO_2. The TC of the sample is subsequently quantified using non-dispersive infrared (NDIR) detection. The TOC of the sample can also be calculated by subtracting the IC from TC (TOC = TC – TIC) [16]. The TOC analyser is often used in CCS research as it provides an easy and sufficient way to measure the CO_2 loading of amine solvents.

3. Conclusions

Studying the degradation and corrosion phenomena related to absorption-based CO_2 capture is a notably challenging task, due to the amount and complexity of the matrix present. A variety of different analytical methods can be utilized to study degraded solvent samples, depending on the targeted compounds. The coupling of different chromatography techniques with mass spectrometry is particularly useful for identifying and monitoring degradation products, however, measurements can be difficult to obtain since these methods are relatively costly and proper calibration is not always possible. Although not as accurate, titration methods are quick, inexpensive and versatile techniques that can sufficiently measure the alkalinity (amine), CO_2 and HSS content of solvent solutions and are very commonly used. Titration (for amine concentration) can also be combined with a TOC analyser to accurately determine the CO_2 loading of a solvent. ICP-MS can be used to detect traces of dissolved metals in the solution and is therefore useful for assessing the corrosivity of aged amine solvents. Collectively these methods can fully characterise a solvent, however, in most cases analytical testing is limited due to practical and economic factors. Experimental testing should be planned considering the capabilities of the available analytical techniques.

4. Further reading

Various open access publications and web pages can help get more information related to degradation monitoring and analyses. Some resources that provide overviews and links to various other references are:

- Evaluation of methods for monitoring MEA degradation during pilot scale post-combustion capture of CO2 - ScienceDirect provides extensive overview of analytical methods often used for degradation monitoring.
- Important Aspects Regarding the Chemical Stability of Aqueous Amine Solvents for CO_2 Capture provides an overview of the status of amine degradation research and is a good source for further references.
- A review of degradation and emissions in post-combustion CO_2 capture pilot plants contains degradation and emission data from various pilot campaigns using amine-based solvents and presents used analytical methods.
- Information package for assessing new amine solvents summarises some of the most important topics when assessing the stability of a new solvent for post-combustion CO_2 capture from various industrial sources.

References

1. Khan, U., et al., *Assessing absorption-based CO2 capture: Research progress and techno-economic assessment overview.* Carbon Capture Science & Technology, 2023. **8**: p. 100125.
2. Li, F., et al., *Modelling of a Post-combustion CO2 Capture Process Using Deep Belief Network.* Applied Thermal Engineering, 2017. **130**.
3. da Silva, E.F., et al., *Understanding 2-Ethanolamine Degradation in Postcombustion CO2 Capture.* Industrial & Engineering Chemistry Research, 2012. **51**(41): p. 13329-13338.
4. Feron, P.H.M., et al., *An update of the benchmark post-combustion CO2-capture technology.* Fuel, 2020. **273**: p. 117776.
5. Buvik, V., *Stability of amines for CO2 capture*. 2021, NTNU.
6. Fytianos, G., S.J. Vevelstad, and H.K. Knuutila, *Degradation and corrosion inhibitors for MEA-based CO2 capture plants.* International Journal of Greenhouse Gas Control, 2016. **50**: p. 240-247.
7. Vevelstad, S.J.a.G., Andreas and Buvik, Vanja and Knuutila, Hanna Katariina and Vernstad, Kai and Wiig, Merete, *Evaluation of Potassium Iodide as Degradation Inhibitor*, in *Proceedings of the 16th Greenhouse Gas Control Technologies Conference (GHGT-16)* 2022.
8. Aronu, U.E., et al., *Impact of heat stable salts on equilibrium CO2 absorption.* Energy Procedia, 2014. **63**: p. 1781-1794.
9. de Hoffmann, E. and V. Stroobant, *Mass Spectrometry: Principles and Applications*. 2013: Wiley.
10. Wang, T. and K.-J. Jens, *Oxidative Degradation of Aqueous 2-Amino-2-methyl-1-propanol Solvent for Postcombustion CO2 Capture.* Industrial & Engineering Chemistry Research, 2012. **51**(18): p. 6529-6536.
11. Freeman, S.A., J. Davis, and G.T. Rochelle, *Degradation of aqueous piperazine in carbon dioxide capture.* International Journal of Greenhouse Gas Control, 2010. **4**(5): p. 756-761.
12. *Nitrosamine Analysis by Gas Chromatography and Agilent 255 Nitrogen Chemiluminescence Detector (NCD) - Technical Overview*.
13. *PerkinElmer Technical Note: ICP-Mass Spectrometry - The 30-Minute Guide to ICP-MS*.
14. *Agilent- ICP-MS Overview*. 02.2025]; Available from: https://www.agilent.com/en/product/atomic-spectroscopy/inductively-coupled-plasma-mass-spectrometry-icp-ms/what-is-icp-ms-icp-ms-faqs.
15. Bade, O.M., et al., *Controlling Amine Mist Formation in CO2 Capture from Residual Catalytic Cracker (RCC) Flue Gas.* Energy Procedia, 2014. **63**: p. 884-892.
16. *Shimadzu-Basics of Total Organic Carbon*. [cited 2025 02.2025]; Available from: https://www.shimadzu.eu/service-support/analysis-basics/total-organic-carbon/index.html#:~:text=IC%20(inorganic%20carbon)%20or%20TIC,dissolved%20CO2%20for%20TIC.