



# A review of gas chromatographic techniques for identification of aqueous amine degradation products in carbonated environments

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## Abstract

Degradation of amines is a significant issue allied to amine-based carbon dioxide (CO<sub>2</sub>) absorption in post-combustion CO<sub>2</sub> capture. It becomes essential to have a detailed understanding of degradation products for advanced post-combustion CO<sub>2</sub> capture technology. Identification and quantification of degradation products of amines help in practicability and environmental assessment of amine-based technology. Gas, liquid, and ion chromatographic techniques are the benchmark tools for qualitative and quantitative analyses of the amines and their derivatives. Among others, gas chromatography has been more in use for this specific application, especially for the identification of degradation products of amines. This review focuses on the critical elucidation of gas chromatographic analysis and development of methods to determine the amine degradation products, highlighting preparation methods for samples and selecting columns and detectors. The choice of detector, column, sample preparation, and method development are reviewed in this manuscript, keeping in view the industry and research applications. Furthermore, obtained results on the quantitative and qualitative analyses using gas chromatography are summarized with future perspectives.

**Keywords** CO<sub>2</sub> capture · Amine degradation products · Gas chromatography · Sample preparation · Column selection · Method development

## Introduction

Elimination of acid gases such as hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) from different industrial and natural gas streams is one of the significant operations taking place in chemical industries (Benamor and Aroua 2007; Park et al. 2006). There are several technologies for CO<sub>2</sub> mitigation such as pre- and post-combustion CO<sub>2</sub> capture and oxyfuel combustion, which further include several other sub-technologies

(Kothandaraman 2010). This also includes conversion of CO<sub>2</sub> into light fuels and chemicals (Mazari et al. 2020c). Plausibly, the amine-based CO<sub>2</sub> absorption-stripping technology represents one of the established and mature options for capturing CO<sub>2</sub> (Blauwhoff et al. 1984; Fredriksen and Jens 2013). The technology involves CO<sub>2</sub> absorption with aqueous amine solutions (Kim et al. 2011; Zaman and Lee 2013). The benchmark amine solvent for CO<sub>2</sub> capture is monoethanolamine (MEA), which is still going through several challenges

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(Saeed et al. 2018). Apart from MEA, several other amines like diethanolamine (DEA), triethanolamine (TEA), piperazine (PZ), methyldiethanolamine (MDEA), 2-amino-2-methylpropan-1-ol (AMP), morpholine (MOR), and several others have been tested separately as well as in blends for CO<sub>2</sub> capture (El Hadri et al. 2017; Ghalib et al. 2017; Pinto et al. 2019). The reaction between amines and CO<sub>2</sub> leads to the formation of several ionic species such as protonated amine, carbamate (RNCOO<sup>-</sup>), bicarbonate (HCO<sub>3</sub><sup>-</sup>), and carbonate (CO<sub>3</sub><sup>2-</sup>). CO<sub>2</sub> absorption in aqueous primary and secondary amine solutions has been described from a mechanistic perspective as well (Caplow 1968; Danckwerts 1979). Danckwerts (1979) proposed the formation of zwitterions produced by the reaction of CO<sub>2</sub> and amines with the removal of base zwitterion protons to form carbamates. The reaction mechanism between amine and CO<sub>2</sub> is likewise a zwitterion mechanism. The lower the pH of CO<sub>2</sub>-loaded solutions, the higher the number of unstable carbamate species. These species hydrolyze to produce bicarbonate and carbonate. The formation of carbonate ions does not occur due to a reason that pH of a system is normally at 7–11 (low basicity). Hence, carbonate-bicarbonate equilibrium reaction tends to shift towards the bicarbonate side (Park et al. 2003).

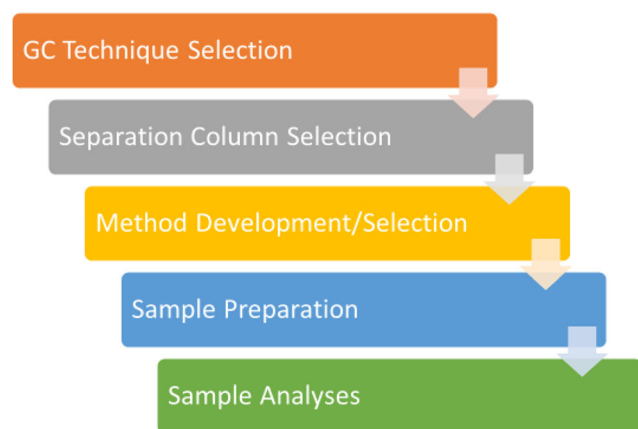
During the acid gas absorption process, amines undergo irreversible reactions while reacting with CO<sub>2</sub>, O<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub> and produce undesired compounds, including nitramines and nitrosamines, which are carcinogenic (Bello and Idem 2005; Jeon et al. 2013; Mazari et al. 2015, 2019). Solvents undergo two types of degradation. The first type is oxidative degradation (Lepaumier et al. 2009a; Rooney and Daniels 1998; Sexton 2008) that mainly occurs due to the presence of oxygen in the gas stream to be treated. The second type is thermal degradation, which takes place at high temperatures (Davis 2009; Lepaumier et al. 2009c). It is well known that secondary amines have better stability than primary amines during the degradation process. Still, reaction routes are not well understood, and the amine structures may have an elusive effect on the stability of degradation products (Riesenfeld and Kohl 1974). Many researchers have proposed the mechanism of CO<sub>2</sub>-induced degradation of traditional alkanolamines at high temperatures. The formation of degradation products from amines decreases their concentration, which reduces the solvent's CO<sub>2</sub> absorption capacity. This causes increased operational cost due to the replacement of solvent in the process (Goff and Rochelle 2006; Huang et al. 2013; Lawal and Idem 2005; Léonard et al. 2014). In addition, the degradation products cause foaming, which increases operational viscosity, corrosion of equipment, and fouling (Ghalib et al. 2020; Mazari et al. 2020b; Ooi et al. 2020; Saeed et al. 2018). Therefore, identification of potential degradation products of amines from post-combustion CO<sub>2</sub> capture (PCCC) is important (Wang and Jens 2012; Wang 2013).

The determination of amine degradation products is not a straightforward process. This is because different combinations of amine types at different operating conditions such as temperature and pressure often result in various degradation products. Additionally, it is reported that components from packing materials used in the contacting equipment add to the complexity. For instance, carbon steel packings have great potential to form metal salts (Stein et al. 1998; Wang et al. 2011). Chromatographic techniques, including gas chromatography (GC), ion chromatography (IC), and liquid chromatography (LC), are the benchmark methods for the detection and identification of degradation products of amines. Some of the common analytical technique combinations used for analyses of degraded amine samples are GC-mass spectrometry (GC-MS), GC-flame ionization detector (GC-FID), IC, liquid chromatography-tandem mass spectrometry (LC-MS/MS), evaporative light scattering detector (ELSD), nuclear magnetic resonance (NMR), etc. However, among others, chromatographic methods are more dominant for identification and quantification of degradation products of amines (Cuccia et al. 2017, 2018).

This study provides an overview of gas chromatographic applications for the identification and quantification of amine degradation products during the CO<sub>2</sub> capture process. To provide readers with an understanding of the use of GC for identifying and quantifying amines and their derivatives, the manuscript highlights the sample preparation methods, selection of column, method development, and sample results on identification and quantification. This study may serve as a guide for the use of gas chromatographic methods for the identification and quantification of amines and their derivatives, focusing on amine-based CO<sub>2</sub> capture technology.

## The analysis of amine degradation products

Several studies on the degradation of amines have reported GC techniques as the workhorse analytical tools for the identification and quantification of degradation products of amines (Lepaumier et al. 2009c, 2011a; Mazari et al. 2016; Saeed et al. 2017). GC has been used with mass spectrometry (MS) and flame ionization detector (FID) as the major detectors. Identification is mostly reported by GC-MS, and sometimes, it is also used for quantification. GC-FID mainly has been used for quantification and, in some cases, for identification as well as in running pre-identified standard samples. GC mostly uses organic solvents like methanol and ethanol, due to the use of the capillary columns for dilution (Chahen et al. 2016). However, in some cases, water is also used for the dilution of samples (Lepaumier et al. 2011b). Figure 1 shows the typical steps involved in the analyses of degraded amine samples using gas chromatography.



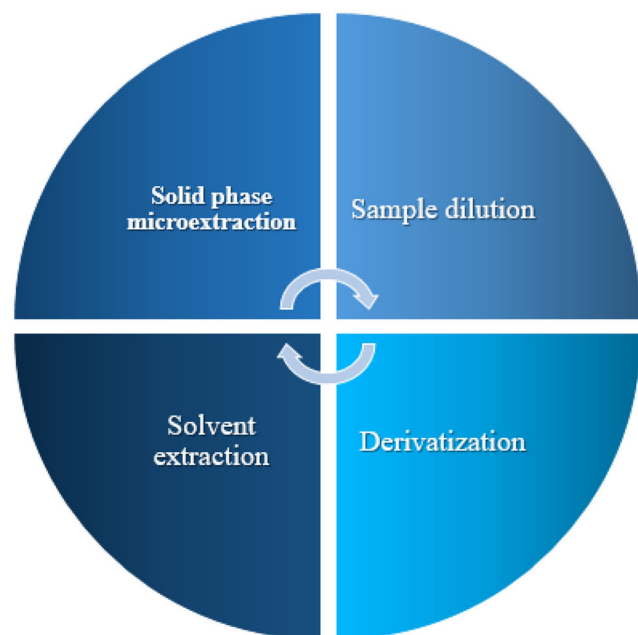
**Fig. 1** Steps involved for the analyses of degraded amines using GC

### Sample preparation methods

Sample preparation for gas chromatographic analyses is an important step. Generally, amine solutions are concentrated, and higher concentrations may indulge and damage the column. Other than dilution depending upon the sample's composition and state, other methods may also be used for the sample preparation. Figure 2 provides a general view of different sample preparation methods for amine samples for gas chromatographic analyses.

#### Sample dilution

Liquid samples must be diluted to prevent the overloading of the column and improve the separation of the compounds



**Fig. 2** Sample preparation methods for degraded amine samples for GC analyses

(Lawal and Idem 2005). Also, the high concentration of amines might pollute the device impacting mass spectrometer recovery (Cuzuel et al. 2015). Mazari et al. (2016) used ethanol to dilute degraded samples of DEA and PZ blend. The dilution factor was based on the concentration of degraded amine samples for analyses, which ranged from 100 to 150 times. Several other studies used similar approaches; however, they used different dilution factors and methods. Lepaumier et al. (2011a) reported that the dilution for analysis depends on two factors: type of analysis and sample degradation level. Supap (1999) used water to dilute degraded MEA samples, which was up to five times the original volume of samples. Most of the authors diluted the samples by organic solvents, and some have used water. However, water has been reported to influence the column life. On the other hand, solvents like methanol or ethanol are found to provide sharp and clear peaks with minimal or no effect on the life of separating column (Johansen 2013; Voice 2013a). Cuzuel et al. (2015) diluted the degraded MEA samples from 10-fold to 1000-fold and found that samples could be diluted at 10-fold to improve the detection limit, thus enhancing the detection of compounds at trace level. Chahen et al. (2016) used methanol for the dilution of analyses of degraded MEA samples.

#### Solvent extraction

Solvent extraction systems involve many stages and are time consuming. It may be used for complex degradation products like amino acids and carboxylic acid (Buch et al. 2006). However, solvent extraction is not common for amine-degraded samples from post-combustion CO<sub>2</sub> processes, rather liquid chromatography is commonly used.

#### Derivatization

Derivatization is a method used for improving the roughness and sensitivity of GC analysis of alkaline analytes, which are thermally labile and strongly polar. Polar amino and hydroxyl groups possess a high affinity for most packing columns, resulting in longer times of elution times, broadening, and asymmetry of peaks. Water is another complicating reason because only certain column packings may tolerate an aqueous amine sample (Kataoka 1996). The extraction of amine and its degradation products with organic solvents have some difficulties with selecting organic solvents. Early studies on the analysis of amine degradation products used derivatization (Brydia and Persinger 1967; Chakma and Meisen 1988, 1997; Choy and Meisen 1980; Kennard and Meisen 1985; Hsu and Kim 1985; Kennard 1983). Derivatization is one of the procedures that can be used to mediate the above problems. The main disadvantages of derivatization methods are (a) inability to form amine derivative in the presence of excess water; (b) incomplete silylation that will result in extra GC peaks, which

are caused by partial silylation of the compounds; (c) long-term instability of derivatives; and (d) high reactivity of reagent and low solubility of degradation products. These disadvantages make applications of amino derivative challenging to be analyzed by GC. Amine extraction from water is often difficult to analyze due to the polarity and formation of hydrogen bonding of water with a column that may damage the column. Amines are adsorbed and decomposed on the column, and this gives tailed elution peaks, weak detector sensitivity, and ghosting phenomena (Knapp 1979). Polarity reductions of amine group and GC property improvement are the basis for derivation methods (Kataoka et al. 2000). It is also a common practice to improve the separation and detection of amines using derivatization reactions. One approach is silylation employed to derivatize –NH and –OH groups in alkanolamines (Kataoka 1996).

Brydia and Persinger (1967) analyzed ethanolamine with a direct GC method, in which the authors experienced problems with peak tailing. The issue was overcome by derivatizing with trifluoroacetyl anhydride to convert a nonvolatile amine into volatile amine trifluoroacetyl derivatives. However, water tends to react with TFA, which causes peak tailing. Piekos et al. (1975) suggested that this drawback may be overcome by converting alkanolamines into trimethylsilyl derivatives. *N,O*-Bis(trimethylsilyl)acetamide (BSA) was used to react with both the amino and hydroxyl groups of alkanolamines. However, this method is limited for a sample with a water content of less than 5%. Also, this method is not applicable when the water content for industrial aqueous alkanolamine is more than 50%. Choy and Meisen (1980) modified the technique by removing water from degraded and fresh alkanolamine through air stripping, followed by derivatization (BSA). This technique is suitable for the analysis of both industrial and laboratory alkanolamine samples. Hsu and Kim (1985) carried out silylation of sample for hydroxy number determinations using 1.0 mL of anhydrous pyridine, 0.2 mL of hexamethyldisilazane, and 0.1 mL of trimethylchlorosilane. The mixture reacted in a screw-cap vial that was shaken vigorously for about 30 s and allowed to remain static for 5 min at room temperature until derivatization was completed. As water is known to cause a problem in GC, Khederlou (2011) developed a method based on extracting the organic phase using a mixed solvent of isopropyl alcohol and ethyl acetate at the ratio of 1:5. Further, the samples were derivatized with BSTFA. The results showed that the number of components and precision in their retention time, as detected by the GC-MS method, increases significantly with the enhanced extraction (Khederlou 2011).

Reynolds et al. (2013) compared the utilization of dehydration and cation exchange methods for cleaning up the degraded aqueous MEA. The dehydration system employed both the molecular sieves and rotary evaporation for removing water from degraded aqueous MEA absorbents. It was observed that

cation exchange removed water and fractionated samples into neutrals and acids (neutral compounds and negatively ionizable compounds) and bases (positively ionizable compounds). The basic, acidic, and neutral fractions were analyzed by GC-MS with and without derivatization. They noticed that dehydration merely removed water from all samples, considering the utilization of water-sensitive derivatization reagents. The main advantage of the dehydration method is that there is less likelihood of loss of strong basic compounds and high molecular weight compounds. Furthermore, unlike the cation exchange method, the dehydration does not remove heat stable salts and nonvolatile compounds from samples. Therefore, dehydrated samples were not analyzed through GC-MS without derivatization. Vevelstad et al. (2013) also identified the degradation products of MEA using gas chromatographic methods as listed in Table 4.

### Solid-phase microextraction

The solid-phase microextraction (SPME) technique was developed early by Arthur and Pawliszyn (1990). It is a solventless sample preparation tool. It combines enrichment, isolation, preparation, and concentration. It aids in overcoming the inherent limitations in the solvent-based sample preparation techniques. Solid-phase microextraction is a sample extraction and a preparation technique that is solvent-free (Abdulra'uf and Tan 2013). However, other researchers applied this approach in the quantification and identification of amine degradation products (Gouedard et al. 2014b; Lu et al. 2009; Rey et al. 2013).

Lu et al. (2009) used SPME technique for the analysis of intermediate photocatalytic degraded products belonging to 2-dimethylamino-2-methyl-1-propanol (DMAMP). For the extraction of DMAMP and intermediates belonging to it, SPME fiber was immersed in the sample solution for about 30 min at room temperature. Magnetic stirring of  $550 \pm 10$  rpm on a stirrer plate was applied. The compounds were then subjected to thermal desorption from the fiber to the GC injector for 25 min. Another study (Cuzuel et al. 2015; Rey et al. 2013) developed a new analytical method based on headspace solid-phase microextraction (HS-SPME). The standards in the method were prepared by spiking a solution of water/ethanolamine (70/30 v/v). The volume of the sample introduced in the 20-mL HS vial was 5 mL for both synthetic and real samples. The procedure is as follows: first, the vial was equilibrated at 70 °C for 5 min. Then, the Carboxen/PDMS fiber was placed into the headspace of the sample for the extraction. The temperature was maintained at 70 °C for 30 min. Finally, the fiber was desorbed directly into the injector set at 250 °C. Contrarily, Gouedard et al. (2014b) developed a method of HS-SPME coupled to GC-MS to identify the degradation products in the MEA system. They identified seven new molecules that were never reported in the literature.



## GC column types

The selection of GC column for the quantifications and identifications of degradation products is crucial. The reasons are the nature and the complexity of degradation products that can be polar and nonpolar. The GC columns involve a flowing mobile phase and a stationary phase, where the stationary is generally known to be the brain of the column and is responsible for separation. A column selection involves the type of stationary phase, the film thickness, inner diameter, and column length (Rahman et al. 2015). Restek® provides detailed guidelines and selection criteria for the columns, which involve data on application-specific stationary phases, choice of Rxi® columns using MS, and choice of general-purpose Rtx® columns. Furthermore, the manufacturer also provides formula, which involves a measure of efficiency, a measure of retention, and peak separation measure for the selection of the best stationary phase. The inside of the capillary column is usually coated with a microscopic layer of liquid or polymer as the stationary phase (Kataoka et al. 2000). The stationary phase interacts with compounds in the analyte up to different degrees. This makes the compounds elute with varying speeds through the column. Retention time is the time taken by a compound to travel through the column. Polarity and molecular weight affect the retention time of compounds. In a specific column, the retention time of a specific molecule can be used to identify the molecule when the conditions are the same (Bruno 2000; Johansen 2013).

Gas chromatography uses two types of columns for separation of the compounds: packed column and capillary column. In comparison to the capillary GC, the packed column GC is easier to set up because of the ability of the stationary phase applied to the solid support and proper modification of the particular analysis (Grob and Barry 2004). One should note that the capillary column contributes to better maintenance and higher sensitivity, offers quicker and more efficient separation, and contributes to the better shape of peak and less samples are required than packed columns (Kataoka et al. 2000). At present, over 90% of analyses are conducted using a capillary column (Polderman and Steele 1956).

### Packed columns

Porous polymer packing also separates degradation compounds. Tenax TA, Tenax GC, and Porapak Q are the most common columns used for separating the amine degradation products. Packed column Tenax GC is a porous polymer which is mainly based on 2,6-diphenyl-phenylene oxide (Voice 2013b). The separation occurs through adsorption on porous polymer and diffusion through the carrier stream. The rate of reaction of the diffusion determines the retention time. Shahi et al. (1994) reported that the short column with Tenax GC packing is suitable for analyzing DEA, MEA, and TEA,

as well as their degradation. However, there are some problems associated with the use of GC for the analysis of hydroxyamines and related compounds. This is due to low vapor pressure, high polarity, and instability at elevated temperatures especially in the presence of metals and the presence of water. Low vapor pressure requires DEA to be subjected at high injector and column temperature. However, it is also speculated that packed column failed to detect the presence of MEA and BHEED. Furthermore, it cannot separate DEA from MDEA or BHEP from HEOD efficiently at low concentrations (Poole and Poole 2012). Shahi et al. (1994) developed a GC technique for the determination of acid gases, amines, and their degradation products and water. The method is based on a combination of Tenax GC and HayeSep Q columns with a switch valve arrangement. The injected sample containing acid gases, water and alkanolamines, and lighter components pass through the HayeSep Q column until H<sub>2</sub>S peak appears. Then, the valve is switched on, and amine is separated in the Tenax GC column.

### Capillary columns

CPSIL8-CB, Carbowax amines, and HP-Innowax are commonly used for the quantification of amines. Various GC stationary phases have been used in order to identify and quantify amine degradation products. The column selections made in the literature are based on the column's polarity, which is an important factor for the separation and detection of degradation products. Some of the columns are good in detecting large variations of degradation products, while others are found only suitable for a few compounds. Therefore, the selection of the right column for analysis is essential to ensure a successful characterization of amine degradation products. To obtain a good separation of components, it is necessary to make use of two different types of the column: polar and nonpolar (Blanc et al. 1982; Lepaumier et al. 2009c). Supap et al. (2006) investigated the detection of MEA oxidative degradation products using different columns. The author found that the overall performance of HP-Innowax was better than HP-35MS and HP-5MS. This column was found to produce acceptable signal peak separations between MEA, water, and other degradation products compared to the other two columns. The authors anticipated the variation of the result of HP-Innowax to the high polarity and capability of column in separating water from MEA and its degradation products. However, HP-35MS (intermediate polarity) was believed to be better than HP-Innowax in analysis degradation products only (Supap et al. 2006). In the same study, the number of detected degradation products by HP-35MS was 16 compared to 14 by HP-Innowax, and only 12 by HP-5MS. Meanwhile, for the intermediate products, a similar trend was observed, where the number of detectable products was reported in the order of HP-35MS (2 peaks) > HP-Innowax = HP-5MS (0 peak) for the MEA/H<sub>2</sub>O/O<sub>2</sub> system, while HP-35MS (3 peaks) > HP-

Innowax = HP-5MS (2 peaks) in the MEA/H<sub>2</sub>O/O<sub>2</sub>/CO<sub>2</sub> system. Hence, HP-35MS can provide the most information on both degradation and intermediate products compared to the other two columns. Besides this, results also suggest that amine degradation products have a wide range of polarities. This means HP-35MS is a viable single column because it has a better detection capability of degradation products.

For the stationary-phase coating used in the columns, polyethylene glycol is the most popular substance with many applications. Table 1 shows the ability of columns coated with polyethylene glycol to detect a wide range of compounds present in the degraded amine samples. Hence, it is evident that the compounds detected by these columns are not identical between each system, proving the claim that amine degradation species of a system is influenced significantly by the system's operating conditions such as the pressure, temperature, and impurities in the amine solution (Choy 1978). Thus, despite the identical coating of active materials in columns, the possibility of error persists. This is due to the variation in the stability of bonding procedures between columns. Furthermore, Dawodu and Meisen (1993) found this difference between Supelcowax 10 and DB-Wax columns. While both columns were coated by polyethylene glycol active material, DB-Wax tolerates lower analysis temperature, which was at 230 °C as compared to Supelcowax 10, which tolerated temperature up to 280 °C due to their different bonding procedures that caused the retention time of the compounds detected by DB-Wax column to be slightly greater than the one

produced by the Supelcowax 10 column. Table 2 provides details on the GC columns used for various amine degradation studies.

However, the application of a single column is always insufficient for detecting all degradation products present in certain systems. It is a common practice to use more than one column to maximize the detection limit of degradation products. Strazisar et al. (2003), for example, used two different columns, like DB-1701 and Nukol™ based on their polarity differences for the detection of degradation products. Expectedly, the results obtained from applying two columns gave unique major signal peaks undetected in another. Figure 3 shows the chromatograms of amine degradation products using two DB-1701 and Nukol™ columns, respectively.

Lepaumier et al. (2011a) also used two columns for the detection of degradation products in their study. They claimed that some compounds were well separated in one column but not in others due to the difference in polarity of the columns. The results suggested that polar Carbowax Amine column was the most suitable for detecting compounds such as DEA and MDEA. In contrast, a nonpolar column of CPSIL8-CB-Amine was more suitable for the detection of high molecular weight degradation products.

Besides the differences in the polarity of chromatography columns, the performance of columns also depends on the type of column. Dawodu and Meisen (1993) reported that the capillary column performs better than the packed column

**Table 1** Packed and capillary and columns with their stationary phases were used in different studies to analyze amine degradation samples

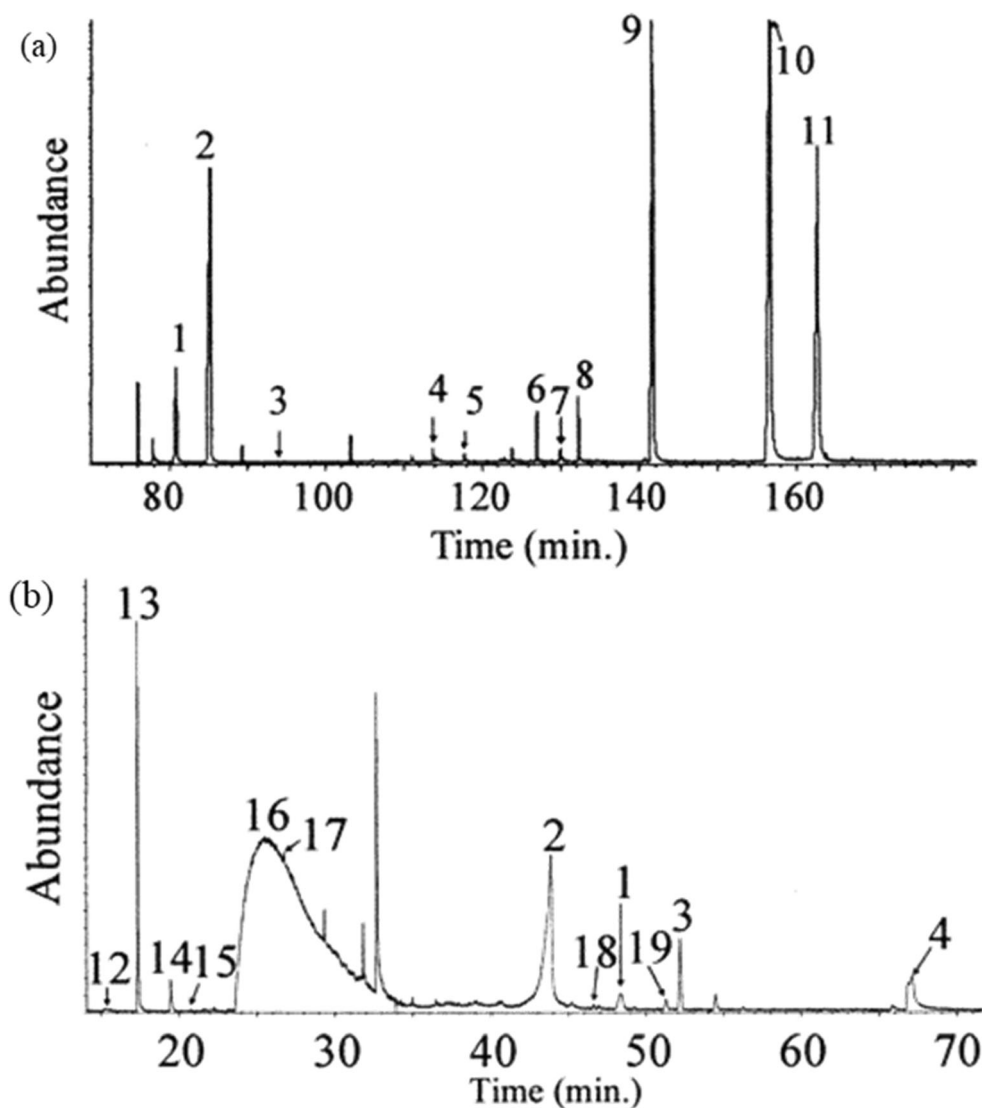
Column	Type	Type of column	Stationary phase	Ref.
Supelcowax 10	WCOT/G	Capillary	Fused silica	(Dawodu and Meisen 1993; Reza and Trejo 2006)
HP-Innowax	WCOT/F	Capillary	Polyethylene glycol	(Bello and Idem 2005; Lawal and Idem 2005; Supap 1999; Supap et al. 2001, 2006)
DB-Wax	WCOT/F	Capillary	Polyethylene glycol	(Dawodu and Meisen 1993)
Nukol™	WCOT/F	Capillary	Modified polyethylene glycol	(Strazisar et al. 2001)
Carbowax amines	WCOT/F	Capillary	Fused silica	(Lepaumier et al. 2009c)
CPSIL8-CB-Amines	WCOT/F	Capillary	5% phenyl polydimethylsiloxane	(Blanc et al. 1982; Lepaumier 2008; Lepaumier et al. 2009a, b, c, 2011a, b)
Tenax TA	WCOT/F	Packed	2,6-Diphenylene oxide	(Dawodu and Meisen 1993, 1996)
Chromosorb W HP	WCOT/F	Packed	8% OV-17	(Choy and Meisen 1980)
DB-1701	WCOT/F	Capillary	14% cyanopropylphenyl-methylpolysiloxane	(Strazisar et al. 2001, 2003)
HP-35MS	WCOT/F	Capillary	5% methyl siloxane	(Supap et al. 2006)
HP-5MS	WCOT/F	Capillary	35% methyl siloxane	(Khederlou 2011; Supap et al. 2006)
HP-17	WCOT/F	Capillary	50% phenyl/50% methyl siloxane	(Dawodu and Meisen 1993)
Rtx-5 Amine	WCOT/F	Capillary	5% diphenyl/95% dimethylpolysiloxane	(Zoannou et al. 2013)
DB-5	WCOT/F	Capillary	5% phenyl/95% dimethylpolysiloxane	(Chahen et al. 2016; Martin et al. 2012; Wang et al. 2011)
Tenax GC	PP	Packed	2,6-Diphenyl-phenylene oxide	(Chakma and Meisen 1988)
Porapak Q	PP	Packed	Stainless steel	(Robbins and Bullin 1984)

WCOT wall-coated open tubular

**Table 2** Summary of different studies using different GC columns and detectors used for analyses of varying amine samples

Ref.	Detector	Column	Length × ID × thickness
(Lepaumier et al. 2009c)	MS + FID	Carbowax amines	15 m × 0.530 mm × 1.0 μm
		CPSIL8-CB-Amines	25 m × 0.320 mm × 1.2 μm
		CPSIL8-CB-Amines	30 m × 0.250 mm × 1.2 μm
		HP-5MS	30 m × 0.225 mm × 0.25 μm
(Lepaumier et al. 2010)	MS + FID	Carbowax amines	15 m × 0.530 mm × 1.0 μm
		CPSIL8-CB-Amines	25 m × 0.320 mm × 1.2 μm
		CPSIL8-CB-Amines	30 m × 0.250 mm × 1.2 μm
		HP-5	30 m × 0.225 mm × 0.25 μm
(Martin et al. 2012)	MS	Carbowax amines	15 m × 0.530 mm × 1 μm
(Rey et al. 2013)	MS	CPSIL8-CB-Amines	30 m × 0.250 mm × 1 μm
		DB-Wax	30 m × 0.250 mm × 0.5 μm
(Lepaumier et al. 2011b)	MS	CPSIL8-CB-Amines	30 m × 0.320 m × 1.0 μm
(Lu et al. 2009)	MS	DB-5	30 m × 0.250 mm × 1.0 μm
(Supap et al. 2006)	MS	HP-5	30 m × 0.250 mm × 0.25 μm
		HP-35	
		HP-Innowax	
(Reynolds et al. 2013)	MS	5% phenyldimethylsiloxane column	30 m × 0.250 mm × 1.0 μm
(Khederlou 2011)	MS	HP-5	30 m × 0.250 mm × 0.1 μm
(Lawal and Idem 2005)	MS	HP-Innowax	30 m × 0.250 mm × 0.25 μm
(Bello and Idem 2005)	MS	HP-Innowax	30 m × 0.250 mm × 0.25 μm
(Supap et al. 2001)	MS	HP-Innowax	30 m × 0.250 mm × 0.25 μm
(Lepaumier et al. 2009a)	MS + FID	Carbowax amines	30 m × 0.530 mm × 1.0 μm
		CPSIL8-CB-Amines	30 m × 0.320 mm × 1.2 μm
		CPSIL8-CB-Amines	30 m × 0.250 mm × 1.2 μm
		HP-5	30 m × 0.250 mm × 0.25 μm
(Al-Thamir 2002)	FID	Chromosorb W HP	1.5 m × 4 mm
(Supap 1999)	MS	HP-Innowax	30 m × 0.25 mm × 0.25 μm
(Dawodu and Meisen 1993)	FID	Tenax TA	2.7432 m × 3.175 mm
		Supelcowax 10	15 m × 0.53 mm × 1.0 μm
		DB-Wax	15 m × 0.53 mm × 1.0 μm
		HP-17	10 m × 0.53 mm × 2 μm
(Strazisar et al. 2003)	MS + FTIR	DB-1701	60 m × 0.32 mm × 0.25 μm
(Mazari et al. 2020a)	MS	Rtx-5MS	30 m × 0.25 mm × 0.25 μm
	FID	CPSIL8-CB	15 m × 0.530 mm × 1 μm
(Saeed et al. 2017)	MS	Rtx-5MS	30 m × 0.25 mm × 0.25 μm
(Chahen et al. 2016)	MS	CPSIL8-CB	30 m × 0.25 mm × 1 μm
	MS	DB-Wax	30 m × 0.25 mm × 0.5 μm
	FID	Carbowax amines	15 m × 0.35 mm × 1 μm
(Cuccia et al. 2019)	MS	CPSIL8-CB-MS	30 m × 0.25 mm, 1 μm
		DB-Wax	30 m × 0.25 m × 0.5 μm
(Lai et al. 2019)	MS	DB-XLB	30 m × 0.25 mm × 0.1 μm
	FID	HP-5	30 m × 0.32 mm × 0.25 μm
(Vu et al. 2019)	FID	Rtx-5 amines	30 m × 0.25 mm × 0.1 μm
(Choi et al. 2020b)	MS	DB-5MS UI	30 m × 0.25 mm × 0.25 μm
(Thompson et al. 2017)	MS	DB-624	60 m × 320 μm × 1.8 μm
(Bontemps et al. 2017)	MS	CPSIL8-CB-MS	30 m × 0.25 mm × 1 μm

**Fig. 3** **a** Chromatogram from DB-1701 column. **b** Chromatogram from Nukol™ column (Strazisar et al. 2003)



in terms of the results peak shape, analysis sensitivity limit, sample size, and reproducibility, even at a lower concentration of samples. However, capillary columns are less durable and expensive compared to packed columns. The polar column allowed detection of compounds like acetic acid, pyrazine, or ethylene glycol (Cuzuel et al. 2015). As explained before, the two columns are complementary to perform efficient and different separations and discover new compounds. A summary of GC columns with their types and stationary phases used to analyze different samples of degraded amines is provided in Table 1.

### GC temperature program

Development, selection, and optimization of the GC sample analysis method are an essential and critical step for analyses of degraded amine samples. Method development involves selecting carrier gas, flow rate, injection temperature, initial

temperature, initial hold time, intermediate temperature, temperature change rate, final temperature, and final hold time. In the gas chromatographic analysis, the oven temperature is believed to influence the operation and results compared to any other single parameter. This is because the parameter could affect the retention time, column pressure drop, flow rate, retention temperature, retention volume, partition coefficient, and the gaseous-liquid diffusion (Revesz et al. 2001). As soon as a liquid sample is injected into GC, it will evaporate into vapor form before it is swept through the column by the mobile phase. However, due to a variation in the boiling point and molecular weights of components in the sample, temperature programming needs to ensure all compounds could evaporate and will be separated in the column (Supap 1999). The concept has further been justified by Revesz et al. (2001) who tested  $C_6$  to  $C_{21}$  hydrocarbons' separation abilities between isothermal and temperature-programmed analysis. Temperature programmed analysis



**Table 3** Summary of various temperature program approaches used for gas chromatographic analysis of amine degradation products in the literature

Type of column	Carrier gas	Flow rate (mL/min)	Oven temperature		Initial hold time (min)	Intermediate temperature (°C)	Change rate (°C/min)	Final temperature (°C)	Final hold time (min)	Ref.
			Injection T (°C)	Initial temperature (°C)						
Tenax TA	He	1	N/S	150	0.5	300	8	300	N/S	(Dawodu and Meisen 1996)
DB-1701	He	1	250	35	N/S	280	1	N/S	N/S	(Strazisar et al. 2001)
Nukol				40		200	5			
HP-Innowax	He	1	N/S	100	0	240	10	240	27	(Lawal and Idem 2005)
Chromosorb W HP	He	1	195	N/S	N/S	142	N/S	142	N/S	(Choy and Meisen 1980)
HP-Innowax	He	1	250	100	1	240	10	240	N/S	(Supap 1999)
HP-Innowax	He	1	N/S	100	10	N/S	10	240	27	(Bello and Idem 2005)
N/S	He	1	270	100	6	120	30	170	48	(Reza and Trejo 2006)
HP-5	He	1	250	50	0.5	N/S	10	320	N/S	(Khederlou 2011)
CPSIL8-CB-Amines	He	1	N/S	40	2	130	7	280	10	(Rey et al. 2013)
DB-Wax	He	1	N/S	40	2	130	7	200	7	
CPSIL8-CB-Amines	He	1	N/S	40	2	210	10	300	10	(Lepaumier et al. 2011b)
HP-Innowax	He	1	250	100	7	N/S	N/S	240	45	(Supap et al. 2006)
HP-35	He	1								
HP-5	He	1								
Rtx-5 Amine	He	1	–	50	0.5	N/S	N/S	320	0.5	(Zoannou et al. 2013)
DB-5	He	1	250	110	10	N/S	N/S	240	10	(Crooks and Donnellan 1989; Martin et al. 2012)
5% phenyldimethylsiloxane	He	N/S	280	60	2	80	12	320	3	(Reynolds et al. 2013)
DB-5	He	N/S	250	40	1	N/S	8	200	4	(Lu et al. 2009)
Tenax GC	N <sub>2</sub>	25	300	150	N/S	N/S	8	300	35	(Alawode 2005)
Tenax GC	N <sub>2</sub>	25	300	100	0.5	N/S	8	300	40	(Chakma and Meisen 1988)
HP-Innowax	He		250	100	1		10	240	5	(Supap et al. 2001)
DB-1701	He	40 and 36 cm/s	250	35	–	–	1	280	–	(Strazisar et al. 2001, 2003)
Nukol				50			5	200		
Carbowax amines	He	3.9	280	60	5	75	8	200	36.4	(Blanc et al. 1982; Lepaumier et al. 2009a, c)
CPSIL8-CB-Amines	He	1.6	280	35	N/S	N/S	N/S	230	30	
CPSIL8-CB-Amines	He	0.9	275	35	N/S	N/S	N/S	230	30	
HP-5MS	He	0.9	280	35	N/S	N/S	N/S	230	30	
Carbowax amines	He		280	60	5	75	8	200	36.4	(Martin et al. 2012)
Chromosorb W HP	He	35	190	65	N/S	N/S	N/S	N/S	N/S	(Al-Thamir 2002)
Tenax GC	N <sub>2</sub>	25	300	150	0.5	N/S	8	300	N/S	(Kennard 1983)
Tenax TA	N <sub>2</sub>	30	300	150	0.5	N/S	8	300	N/S	(Dawodu and Meisen 1993)

**Table 3** (continued)

Type of column	Carrier gas	Flow rate (mL/min)	Oven temperature			Ref.			
			Injection T (°C)	Initial temperature (°C)	Initial hold time (min)	Intermediate temperature (°C)	Change rate (°C/min)	Final temperature (°C)	Final hold time (min)
Supelcowax 10			280	125	0.5		8	275	N/S
DB-Wax			300	125	0.5		8	230	N/S
HP-17			300	125	0.5		8	280	N/S
Elite-5MS	He			50	0.5	–	–	320	N/S
DB-Wax			280	70	0	150	10	230	10
CPSIL8-CB-Amines	He		280	40	2	130	13	280	10
DB-Wax				40	2	130	10	200	7
OPTIMA-35MS	He			35	2	140	5	240	8
Tenax GC	He	30	280	35	1		30	280	
HayeSep Q									
CPSIL8-CB-MS	He	1	NS	40	2	130	7	280	10
DB-Wax		1	NS	40	2	130	7	200	10
CPSIL8-CB	He	1	250	40	2	130	13	280	7
DB-Wax	He	1	250	40	2	130	7	200	7
Carbowax amines	He	8	250	100	8	–	–	200	5
	He	1	300	70	1	–	–	240	10
CPSIL8-CB-MS	He	1	280	40	2	130	13	280	10
DB-Wax	He	1	250	120	–	–	7	240	10
DB-624	He	2	200	80	2	–	10	240	4

resulted in better separation of compounds than isothermal analysis, especially for high boiling point molecules ( $C_{15}$  as an example). The isothermal analysis approach gives a relatively large retention time, while the signal peak is quite broad. A summary of various temperature program approaches reported in the literature is exhibited in Table 3.

### Selection of detectors

A detector analyzes the separated compounds by the columns. It detects and delivers information on the separated degradation products. However, the compounds present in the sample take different times to reach the detector. This is a sign of good compound partitioning in the GC column. The signals that arrive from the detector are then converted into useful information and ready for further interpretation. The standard detectors in gas chromatography for analysis of amine degradation products are FID and MS.

#### Gas chromatography-flame ionization detector

The GC-FID detector is robust and easy to use and has good sensitivity for amine degradation products and a wide linear response range. Initially, in GC-FID, effluent is mixed with hydrogen and air and then ignited to produce electrons and ions conducting electricity through the flame. An electric potential is applied at the tip of the burner, where the collector electrode is positioned closely above the flame. The resulted currents are measured and converted into peaks. It is also the earliest detector employed for the analysis of amine degradation products. However, it is limited to the separation of amines by using unlike packed columns, where tedious derivatizations are necessary for the analysis (Brydia and Persinger 1967).

#### Gas chromatography-mass spectrometry

The introduction of GC-MS has successfully overcome the limitation of GC-FID by providing a secondary source of identification during its operation. MS offers quantitative analysis with high sensitivity and selectivity (Xiao et al. 2012). The advent of the mass spectrometer resolves the difficulty of separating compounds with similar retention times. Hence, it has obtained vast attention. The features like great sensitivity and electron impact MS libraries curlicue and its usage. An electron impact source is time privileged, and the standard ionization technique is used for all kinds of GC-MS analysis of degradation products of amines. At 70 eV ionization energy and 200–250 °C temperature, the electrons are emitted continuously from the heated filament and get collided with the targeted gaseous compounds eluted from the end of the GC column for producing molecular ions (if available) and fragment ions for each molecule (Hao et al. 2007). Cuzuel et al. (2015) developed GC-MS procedure to detect amine

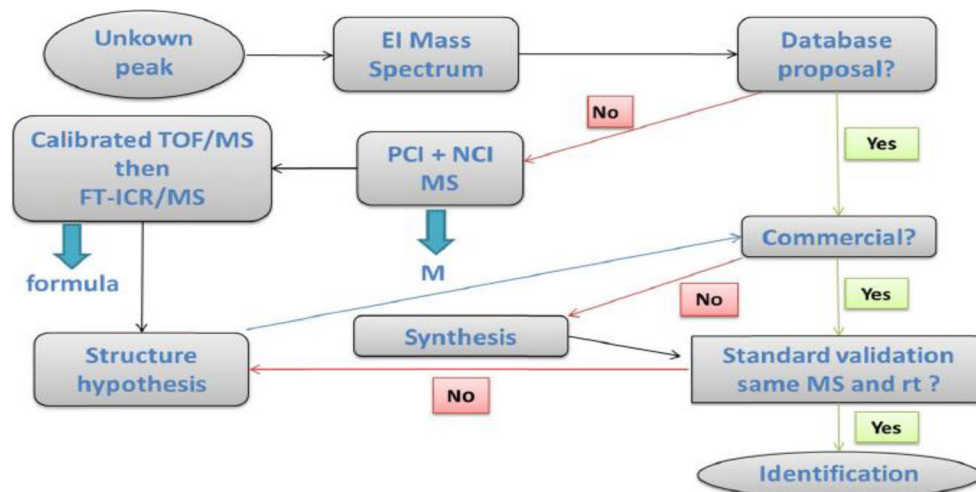
CO<sub>2</sub> degradation products. Briefly, in the first place, the molecular weight of degradation products was determined by using GC-MS-time of flight (TOF), which allowed to obtain the exact mass and confirm the exact mass FT-ICR-MS was used. Additionally, some degradation products were synthesized. The procedure is illustrated in Fig. 4.

### Sample results of GC analyses for degradation products of amines

In large-scale operations, amine degradation reactions are even more complex and difficult to understand due to the presence of many unknowns other than the parameters that could be monitored during the operation. Lepaumier et al. (2011a) compared chromatographic results of samples analyzed from Esbjerg pilot plant in Denmark and laboratory experimental results and found discrepancies in terms of the degradation products detected during its operation. The degradation of MEA in pilot scale was found to produce new compounds such as (include full names) oxazolidin-2-one (OZD), 1-(2-hydroxyethyl)formamide (HEF), *N*-(2-hydroxyethyl)imidazole (HEI), *N*-(2-hydroxyethyl)imidazolidin-2-one (HEIA), 2-hydroxy-*N*-(2-hydroxyethyl)acetamide (HHEA), 1-(2-hydroxyethyl)acetamide (HEA), *N*-(2-hydroxyethyl)piperazin-3-one (HEPO), *N*-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide (HEHEAA), and *N,N'*-bis(2-hydroxyethyl)oxalamide (BHEOX), which were not detected during its laboratory analysis. Reynolds et al. (2013) reported some findings from the analysis of 30% MEA solvent sampled using GC-MS during operation at coal-fired power station post-combustion capture (PCC) pilot plants at Tarong and Loy Yang Power operated by CSIRO. They found that the MEA degradation products identified during laboratory-scale trials were also produced during pilot-scale PCC. Strazisar et al. (2003) identified the major MEA degradation pathway from the IMC Chemicals Facility in Trona, CA, by GC-MS and GC-FTIR. However, the result obtained had not been observed in laboratory experiments. Study reported the role of carboxylic acid in enhancing the degradation of MEA into amide derivatives such as HEF, HHEA, HEA, and BHEOX compounds. da Silva et al. (2012) used GC-MS to compare the degradation of MEA in the lab-scale and three pilot plants, namely Longannet (UK), Tiller (Norway), and Esbjerg (Denmark). A few similarities of degradation products from lab-scale and pilot plants were observed.

Thompson et al. (2017) investigated 5 m MEA under pilot plant CO<sub>2</sub> capture campaigns for a 0.7-MWe plant. Apart from several other techniques, authors also used GC-MS for analyses of degradation products of MEA. Analysis was performed on Agilent 7890A GC with a 7693 auto sampler and 5975C EI/MSD, and DB-624 column was used. Study reports quantification and identification of several nitrosamines, for

**Fig. 4** GC-MS strategy developed by Cuzuel et al. (2015) to detect amine degradation products



example *N*-nitrosodibutylamine (NDBA), *N*-nitrosodiethylamine (NDEA), *N*-nitrosodipropylamine (NDPA), *N*-nitrosomorpholine (NMOR), *N*-nitrosopyrrolidine (NPY), etc. Handojo et al. (2018) studied the non-oxidative thermal stability of MDEA, MEA, and their blends by using GC-MS/FTIR spectra. The GC-MS analysis was carried on Shimadzu GCMS-QP-2010 with Rtx-5 Amine capillary column. Study reported the quantification of loss of MDEA, MEA, and their blends robustly, which were validated through density functional theory (DFT) functional calculations. Cuccia et al. (2019) reported the degradation of the blend of MDEA/MEA (5/25 wt%) for CO<sub>2</sub> capture on a pilot developed by EDF R&D France named as EMEDES-CO<sub>2</sub> lab-scale pilot plant (Bontemps et al. 2014). The system is designed to reproduce the dynamic cycling of the solvent between the absorber and the stripper columns through chemical absorption principle and short cycles of absorption and desorption. The system also includes fast heating and cooling. An experimental campaign of 900 h was run at an average CO<sub>2</sub> loading of 0.12 mol/mol and 0.40 mol/mol amine at lean and rich solvents, respectively. The solvent degradation was monitored using various analytical setups including GC-MS. The study used Agilent 7890A coupled with an Agilent 5975C inert XL MSD. A MultiPurpose Sampler (MPS) auto sampler was attached, which enabled HS-SPME, fully automated liquid injections, and thermodesorption analyses. CPSIL8-CB-MS, which is a nonpolar-fused silica capillary column, and DB-Wax, a polar-fused silica capillary column, were used for the analyses. Authors reported identification of 8 compounds through GC-MS analyses.

Karnwiboon et al. (2019) modified OH aliquot mixed with 2-ethyl-1-hexanol to separate formate, glycolate, oxalate, imidazole, 2-oxazolidone, *N*-(2-hydroxyethyl)succinimide, and *N*-acethylethanolamine, from MEA, AMP, MDEA, and their blends. GC-FID was used with DB-Wax with cross-linked polyethylene glycol with dimensions of 5 μm × 150 mm × 4.6 mm for identification of *N*-(2-hydroxyethyl)succinimide)



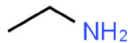
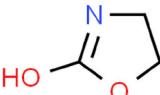
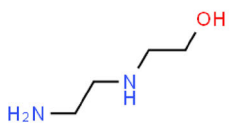
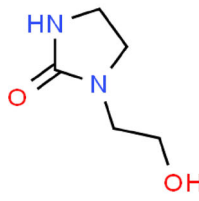
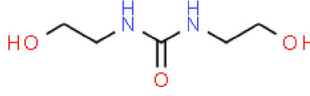
and *N*-acethylethanolamine. Lai et al. (2019) proposed an energy-efficient amine regeneration process that includes the regeneration of rich amine by using amine with alcohols instead of water as a solvent. The regeneration of the MEA containing 40 wt% ethanol, 20 wt% MEA, and 20 wt% H<sub>2</sub>O was effectively achieved at 75 °C, which is an improvement of up to 236 times in CO<sub>2</sub> desorption rate as study suggests. Due to low temperature, a fewer degradation product was formed, which was identified and quantified by using GC-MS and GC-FID. The Agilent 7890A GC system was equipped with an auto sampler, FID was used with HP-5 column, whereas GC-MS analysis was performed on an Agilent 7890B GC system with an auto sampler, Agilent 2977B MSA mass spectrometer, and DB-XLB column. Authors reported no degradation products using ethanol as the solvent; however, GC detected degradation products like *N*-(2-hydroxyethyl)-ethylenediamine (HEEDA), 1-(2-hydroxyethyl)piperazin-2-one (1HEPO), 4-(2-hydroxyethyl)piperazin-2-one (4HEPO), and HEIA, for water-based solutions when heated at 125 °C for 120 h.

Apart from typical aqueous amine-based systems for CO<sub>2</sub> capture, amine-functionalized or hybrid systems are also being explored for CO<sub>2</sub> absorption, adsorption, and reduction (Bhattacharya et al. 2020; Guo et al. 2020; Voskian et al. 2020). The need of quantification and identification of amine and their degradation products is equally important therein as well. Vu et al. (2019) investigated the oxidative deterioration of tetraethylenepentamine-impregnated silica sorbents for CO<sub>2</sub> capture. GC-FID was performed on Shimadzu GC 2010 instrument by using Restek column Rtx-5 Amine for concentration determination of TEPA. Another study by Mancuso et al. (2020) reported the application of GC-MS for the catalytic carboxylation of homopropargylic amines to 6-methylene-1,3-oxazin-2-ones. The study reports identification of several products by using GC-MS. The amines and their derivatives are also found in the atmosphere and in the water bodies. Choi et al. (2020b)

determined the atmospheric amines at Seoul, South Korea, using GC-MS. Authors used Agilent 7890B GC, equipped with a triple quadrupole mass spectrometer (MS-MS) system using a DB-5MS UI column. Study reported identification and quantification of several amines, such as dimethylamine (DMA), DEA, butylamine (BA), propylamine (PA), and

ethylamine (EA), and their derivatives like nitrosodimethylamine (NDMA), NDEA, diethylnitramine (DEN), and dimethylnitramine (DMN). Similarly, another study of Choi et al. (2020a) also reported the use of GC/MS-MS for the detections of amines and their derivatives. Not all but a comprehensive summary of various degradation

**Table 4** Summary of degradation products of some common amines determined by the different methods of GC

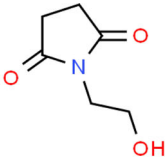
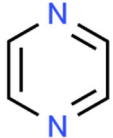
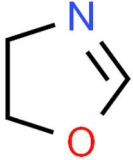
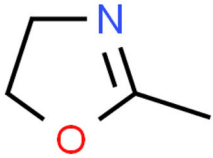
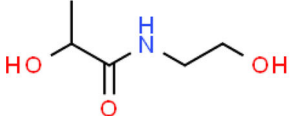
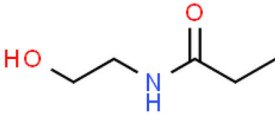
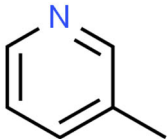
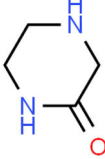
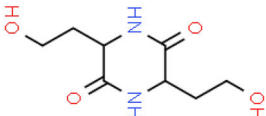
Amine+ references	Name of Degradation Products	Detectors		Chemical structure of Degradation products
		MS	FID	
MEA (Vevelstad et al. 2013)	Methylamine	x		
MEA (Vevelstad et al. 2013)	Dimethylamine	x		
MEA (Vevelstad et al. 2013)	Ethylamine	x		
MEA (Lepaumier et al. 2011a, Lepaumier et al. 2009c, Strazisar et al. 2001, 2003)	Oxazolidin-2-one	x	x	
MEA (Lepaumier et al. 2011a, Lepaumier et al. 2009c, Supap et al. 2006)	N-(2-hydroxyethyl)ethylenediamine	x	x	
MEA (Lepaumier et al. 2011a, Lepaumier et al. 2009c, Supap et al. 2006)	Hydroxyethyl imidazolidinone	x		
MEA (Lepaumier et al. 2011a)	Bis-(2-hydroxyethyl)urea	x		



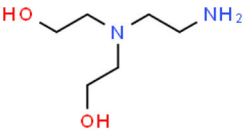
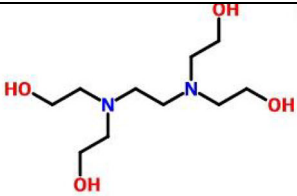
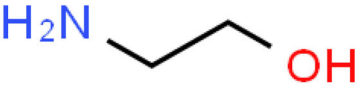
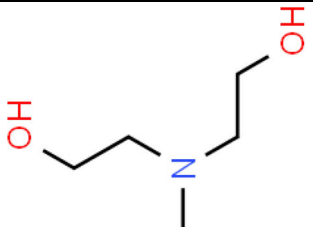
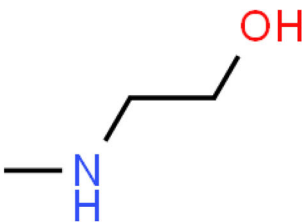
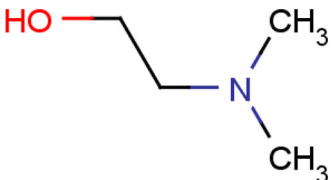
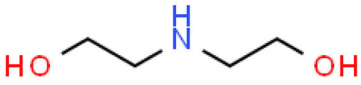
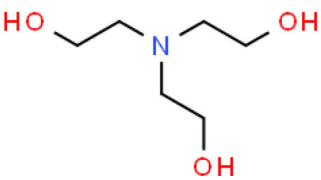
**Table 4** (continued)

MEA (Lepaumier et al. 2011a, Supap et al. 2011)	2-Hydroxy-N-(2-hydroxyethyl)acetamide	x		
MEA (Strazisar et al. 2001, Supap et al. 2006)	N-glycylglycine	x		
MEA (Strazisar et al. 2003)	1-(2-hydroxyethyl)-formamide	x		
MEA (Lepaumier et al. 2009a, Supap et al. 2011)	[(2-Hydroxyethyl)amino](oxo)acetic acid	x		
MEA (Lepaumier et al. 2011a, Lepaumier et al. 2009a, Strazisar et al. 2003, Supap et al. 2011)	4-(2-Hydroxyethyl)-2-piperazinone	x		
	Piperazin-2-one	x		
	N-nitrosomorpholine	x		
MEA (Lepaumier 2008)	N,N'-bis(2-hydroxyethyl)ethylenediamine			
MEA (Lepaumier et al. 2011a, Supap et al. 2011)	N,N'-bis(2-hydroxyethyl)oxalamide	x		

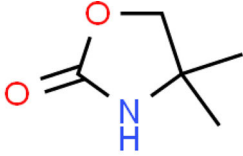
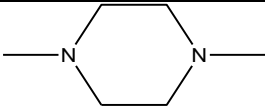
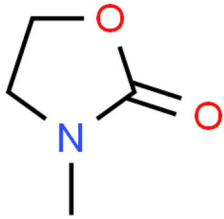
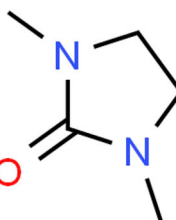
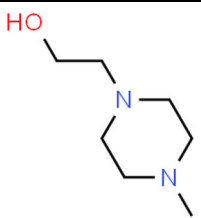
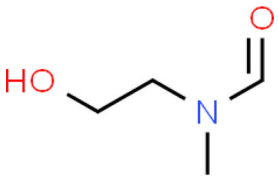
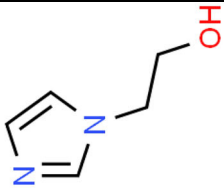
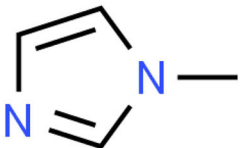
**Table 4** (continued)

MEA (Rooney et al. 1998, Supap et al. 2011)	N-(2-hydroxyethyl)- succinimide	x		
MEA (Rey et al. 2013)	Pyrazine	x		
MEA (Rey et al. 2013)	Oxazoline	x		
MEA (Rey et al. 2013)	2-Methyloxazoline	x		
MEA (Rey et al. 2013)	N-(2- hydroxyethyl)lactamide	x		
MEA (Rey et al. 2013)	N-(2- hydroxyethyl)propanamid e	x		
MEA (Rey et al. 2013)	3-Picoline	x		
MEA (Rey et al. 2013)	2-Oxopiperazine	x		
MEA (Rey et al. 2013)	3,6-di(2- hydroxyethyl)piperazine- 2,5-dione	x		

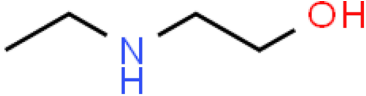
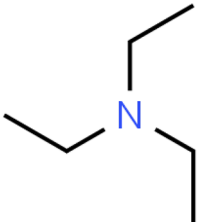
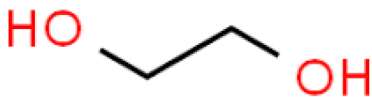
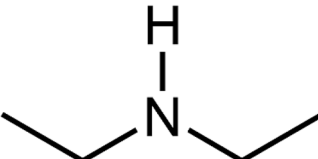
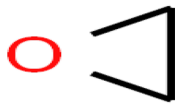
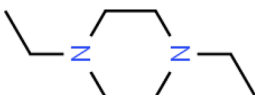
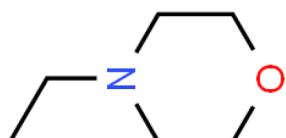
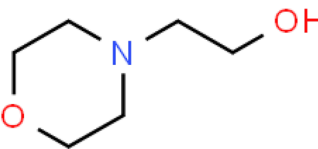
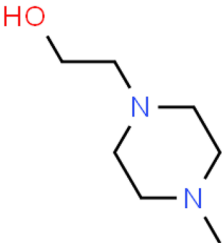
**Table 4** (continued)

DEA (Kennard 1983)	2,2'-[(2-Aminoethyl)imino]diethanol	x		
DEA (Kennard 1983) MDEA (Chakma & Meisen 1997)	N,N,N',N'-Tetrakis(2-Hydroxyethyl)Ethylendiamine	x		
DEA (Kennard 1983)	Monoethanolamine	x		
DEA (Lepaumier 2008)	N-methyldiethanolamine	x		
MDEA (Chakma & Meisen 1988)	N-methylethanolamine	x	x	
MDEA (Chakma & Meisen 1988)	N,N-Dimethylethanolamine	x	x	
MDEA (Chakma & Meisen 1997)	Diethanolamine	x		
MDEA (Chakma & Meisen 1988)	Triethanolamine	x	x	

**Table 4** (continued)

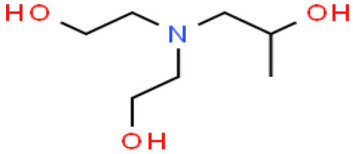
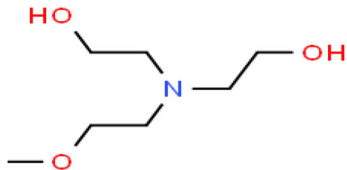
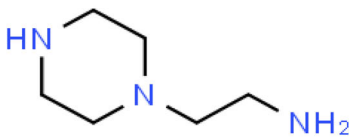
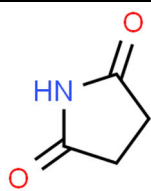
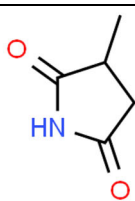
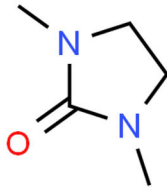
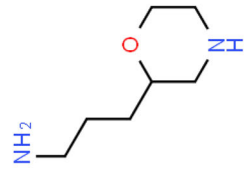
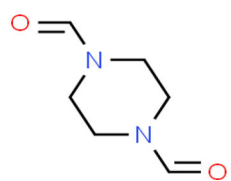
AMP (Lepaumier 2008, Wang & Jens 2012b)	4,4-Dimethyl-1,3-oxazolidin-2-one	x		
MMEA (Lepaumier et al. 2011b)	N,N'-dimethylpiperazine	X		
MMEA (Lepaumier et al. 2011b)	N-Methyloxazolidone	X		
MMEA(Lepaumier et al. 2011b)	1,3-Dimethyl-2-imidazolidinone	X		
MMEA (Lepaumier et al. 2011b)	1-(2-Hydroxyethyl)-4-methylpiperazine	X		
MMEA (Lepaumier et al. 2011b)	N-(2-Hydroxyethyl)-N-methylformamide	X		
MMEA (Lepaumier et al. 2011b)	1-(2-Hydroxyethyl)imidazole	X		
MMEA (Lepaumier et al. 2011b)	1-methylimidazole	X		

**Table 4** (continued)

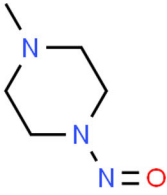
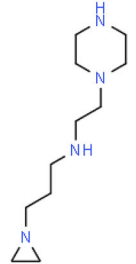
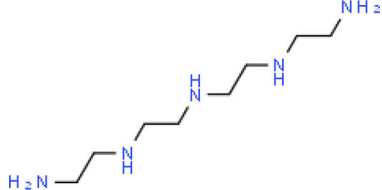
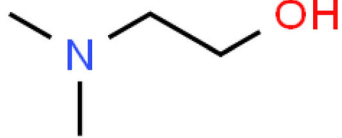
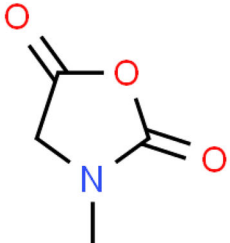
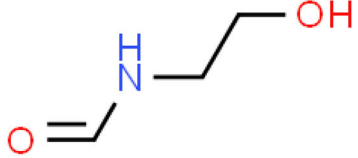
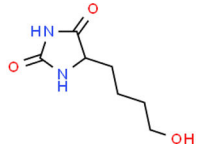
DEEA (Gao et al. 2015)	N-ethylethanolamine	X		
	Triethylamine	X		
	Ethyleneglycol	X		
	Diethylamine	X		
	Ethyleneoxide	X		
	N,N-diethylpiperazine	X		
	N-ethylmorpholine	X		
DEA (Saeed et al. 2019)	2-Morpholinoethanol	X		
	2-(4-Methyl-1-piperazinyl)ethanol	X		



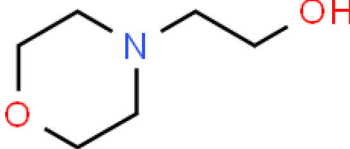
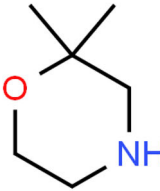
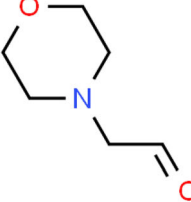
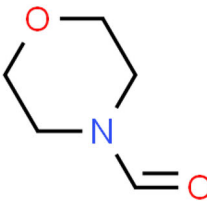
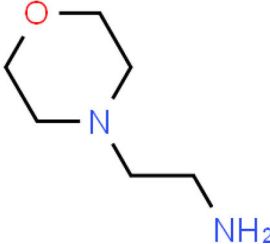
**Table 4** (continued)

	1-[Bis(2-hydroxyethyl)amino]-2-propanol	X		
	2,2'-[(2-Methoxyethyl)azanediyl]diethanol	X		
	1-Piperazineethanamine	X		
AEEA (Saeed et al. 2017)	Succinimide	X		
	N-Methylsuccinimide	X		
	N,N'-Dimethyl-2-imidazolidinone	X		
	(3-Aminopropyl)morpholine	X		
	1,4-Diformylpiperazine	X		

**Table 4** (continued)

	1-Methyl-4-nitrosopiperazine	X		
	3-(1-Aziridiny)-N-[2-(1-piperazinyl)ethyl]-1-propanamine	X		
	Tetraethylenepentamine	X		
	N,N-Dimethylethanolamine	X		
	3-Methyl-1,3-oxazolidine-2,5-dione	X		
	N-(2-Hydroxyethyl)formamide	X		
MOR (Mazari et al. 2020a)	5-(4-Hydroxybutyl)-2,4-imidazolidinedione	X		

**Table 4** (continued)

	2-Morpholinoethanol	X		
	2,2-Dimethylmorpholine	X		
	4-Morpholinylacetaldehyde	X		
	N-Formylmorpholine	X		
	4-(2-Aminoethyl)morpholine	X		

products of amines identified through gas chromatographic methods is provided in Table 4.

## Conclusions and perspectives

Gas chromatography is a powerful method used to identify and quantify amines and their degradation products. The gas chromatography equipment includes the use of several sophisticated parts, for example the injector, heating oven, detector,

and separation column. Identification and quantification of amines and their derivatives depend on the separation column and method used. Before injecting the sample into the column for separation, samples are prepared for use through dilution, derivatization, extraction, etc. One of the powerful tools for sample preparation and use is headspace solid-phase microextraction. Method development is based on the type of sample, the selected relevant column, and playing around with temperature. Studies indicate that the most used detector to quantify and identify amine degradation products is mass

spectrometry. Furthermore, GC-MS/MS is more sensitive for the identification of compounds. Capillary columns are more commonly used; organic solvents are in more use for the dilution of samples. There is no all-in-one best column for characterizing amine degradation products. This is because selecting the most appropriate column for analysis is mainly dependent on the species present in the amine degradation products. Despite the advantages of GC for the analysis of amine degradation products, there are still some challenges that need to be addressed. An imperative limitation of analytical equipment is the possibility of several degradation products evading detection and, hence, remaining unknown. This may be solved through proper sample preparation, choice of the most relevant column, and playing around with the analytical method. Furthermore, there is need of development and intergradation of different sampling techniques, detectors, GC columns, and analysis methods.

**Author contributions** Idris Mohamed Saeed, Shaukat Ali Mazari, Peter Alaba, Brahim Si Ali, Badrul Mohamed Jan, Wan Jeffrey Basirun, Yahaya Muhammad Sani, Sabzoi Nizzamuddin, and Nabisab Mujawar Mubarak contributed to the review and article writing.

**Data availability** This section is not applicable.

## Compliance with ethical standards

**Competing interests** The authors declare that they have no competing interests.

**Ethical approval** This section is “not applicable” for this study as the study does not involve any human participants nor their data or biological material.

**Consent to participate** This section is “not applicable” for this study as the study does not involve any human participants nor their data or biological material.

**Consent to publish** This section is “not applicable” for this study as the manuscript did not include any data from individuals.

## Nomenclature

**Symbols** °C, degree Celsius; ml, milliliter

**Acronyms and abbreviations** AEEA, 2-(2-aminoethylamino)ethanol; AMP, 2-amino-2-methyl-1-propanol; BHEEDA, *N,N*-bis(2-hydroxyethyl)ethylenediamine; BHEOX, *N,N*-bis(2-hydroxyethyl)oxalamide; BHEP, 2,2'-(piperazine-1,4-diyl)diethanol; BSA, *N,O*-bis(trimethylsilyl)acetamide; BSTFA, *N,O*-bis(trimethylsilyl)trifluoroacetamide; DEA, diethanolamine; EI, electron impact ionization; FID, flame ionization detector; FTIR, Fourier transform infrared spectroscopy; GC, gas chromatography; HEA, *N*-(2-hydroxyethyl)acetamide; HEEDA, *N*-(2-hydroxyethyl)-ethylenediamine; HEF, *N*-(2-hydroxyethyl)formamide; HEHEAA, *N*-(2-hydroxyethyl)-2-(2-hydroxyethylamino)acetamide; HEI, *N*-(2-hydroxyethyl)imidazole; HEIA, *N*-(2-hydroxyethyl)imidazolidin-2-one; HEOD, hydroxyethyl oxazolidinone; HEPO, *N*-(2-hydroxyethyl)piperazin-3-one; HHEA, 2-hydroxy-*N*-(2-hydroxyethyl)acetamide; MDEA, *N*-

methyldiethanolamine; MEA, monoethanolamine; MMEA, *N*-methylethanolamine; MS, mass spectrometry; OZD, 2-oxazolidone; PCC, post-combustion capture; PZ, piperazine; THEED, *N,N,N'*-tris(2-hydroxyethyl)ethylenediamine; WCOT, wall-coated open tubular

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