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Tandem Mass Spectrometry of Alkanolamines in Environmental Samples

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1. Introduction

Alkanolamines are anthropogenic compounds used extensively not only in the processing of sour natural gas but in other operations such as the petrochemical and fossil-fuel fired industries to reduce and prevent the emission of green house gases into the environment. Alkanolamines also find uses as corrosion inhibitors, emulsifying agents and in pharmaceutical formulations (Dobberpuhl and Johnson, 1995). Over many years of operation, there have been inadvertent leaks of these chemicals from the surrounding gas processing facilities to groundwater, wetlands soil, and associated uptake by vegetation (Luther et al., 1998; Headley et al., 1999; Hamborg et al., 2011). Since alkanolamines are highly water miscible (Davis and Carpenter, 1997), their analysis has presented some challenges (Jagota et al., 1996) particularly the requirements for suitable extraction from biological matrices and soil, along with sensitive detection using commonly available instrumentation. Early methods of analyzes were focused on direct determination of the analytes with little or no derivatization steps (Witzaney and Fedorak, 1996). Alkanolamines were determined primarily using gas chromatography (GC) with flame ionization (FI) or mass spectrometric (MS) detection (Shahi et al., 1994; Dawodu and Meisen, 1991, 1994, Niitsue et al., 1993 as cited in Peru et al., 2004). Positive-ion electrospray ionization tandem mass spectrometry (ESI-MS-MS) is well suited for the confirmation of uptake of alkanolamines and transformation products in wetland vegetation (Headley et al., 1999). The objective of this chapter is to enumerate the use of tandem mass spectrometry for the determination of alkanolamines from environmental samples exemplified by wetland vegetation.

2. Occurrence and uses of alkanolamines

In the last 25 years, alkanolamines have been studied extensively because of their industrial importance in natural gas processing plants, synthetic ammonia plants, fossil-fuel-fired power plants, chemical, and petrochemical industries (Mundhwa and Henni, 2007). Alkanolamines are used as chemical intermediates and as surface-active agents in cosmetics, pharmaceuticals, agricultural products, and in various industrial products and applications. Aqueous solutions of alkanolamines are commonly used on a large scale in the natural gas industry to strip and remove acid gases such as carbon dioxide, sulfur dioxide and

hydrogen sulfide) from natural gases and hydrocarbon liquids (Carroll and Marther, 1997; Kohl and Nielsen, 1997 as cited in Hansen et al., 2010). Other uses and applications of alkanolamines are summarized in the Table 1.

Application	Function	Type of alkanolamines
Coating	Used in both water and solvent based coatings. Increase the solubility of other components and enhance solution stability	DEEA and DMEA
Emulsifying and Dispersing agents	Emulsifying additives in textile, lubricants, polishes, detergents, pesticides and personal care products – hand lotions, shaving creams and shampoos.	Fatty acid soaps of DEEA and DMEA
Gas Treating agents	Stripping of undesirable gases such as SO_2, CO_2,H_2S during natural and refinery processes	MEA, DEA, TEA, DIPA*
Pharmaceuticals	Used as intermediates for the production of active pharmaceutical ingredients	DMEA – synthesis of procanine and procaine penicillin G, Tamoxifen DMEA and MEA – synthesis of antihistamines.
Catalysts	Promotes foam rise and gel strength properties in the production of urethane foam used in refrigerator and other insulation applications	DMEA
Water Treatment	Used widely in the production of water treatment products such as water-soluble polymeric flocculants and ion exchange resins and corrosion inhibitors	DMEA

Table 1. Uses and application of alkanolamines [DOW Application note (2003); *Shih et al., 2002]. The acronyms: MEA, DEA, TEA, DIPA, DEEA, DMEA are defined below in Figure 1.

3. Structure and classification of alkanolamines

Alkanolamines can be classified according to the number of alkyl groups bonded to the nitrogen atom of the amino group as: (1) Primary e.g. diglycolamine (DGA); monoethanolamine (MEA); monoisopropanolamine (MIPA); (2) Secondary e.g. diethanolamine(DEA); diisopropanolamine (DIPA); (3) Tertiary e.g. diethylethanolamine (DEEA), dimethylethanolamine (DMEA), methyldiethanolamine (MDEA), triethanolamine (TEA); and (4) sterically hindered amine, 2-amino-2-methyl-1-propanol (AMP) (Padurean et al., 2011). In accordance with the convention used in the alkanolamine literature (Jamal et al., 2006 as cited in Padurean et al., 2011), MEA is represented as R_1NH_2,, where R_1 signifies CH_2CH_2OH; DEA is represented as R_1R_2NH, where R_1-R_2 denotes CH_2CH_2OH; MDEA is

represented as R_1R_2 R_3NH, where R_1-R_2 implies CH_2CH_2OH and R_3 is CH_3; AMP is represented as R_4NH_2 where R_4 is $-C(CH_3)_2CH_2OH$ (Metz et al., 2005; Gibbins and Chalmers, 2008 as cited in Padurean et al., 2011). Chemical structures of some common alkanolamines are given in Figure 1. Of all the alkanolamines four are commonly used for capture of CO_2 from industrial processes of fossil fuel. They are MEA, DEA, MDEA, AMP, (Libralato et al., 2010; Padurean et al., 2011). Padurean et al., (2011), expounded on the criteria on which, the consideration was based. A less common alkanolamines that is also used in the acid gas removal from natural gas industry is 2-piperidinethanol (2-PE) (Shih et al., 2002). Table 2 presents some of the physical properties of common alkanolamines.

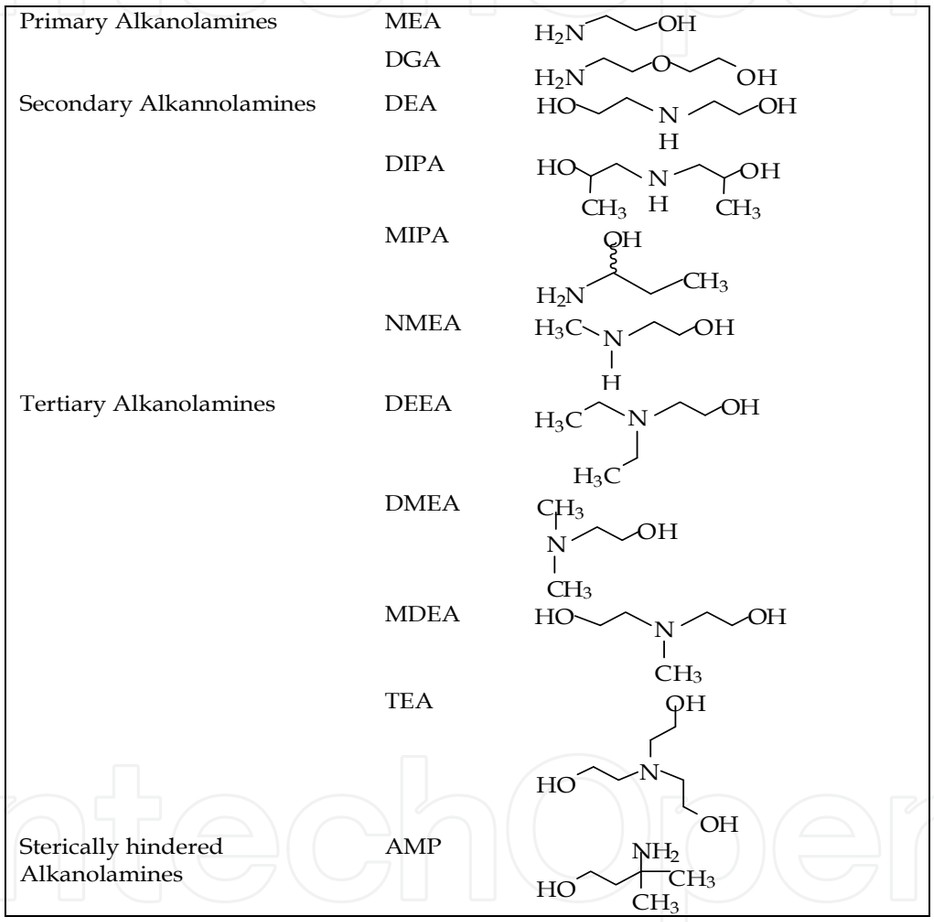

Fig. 1. Chemical structures of some common alkanolamines.

4. Production and environmental distribution

In 1993, approximately 20 million kg of alkanolamines were used for natural gas purification in the United States (Hawthone et al., 2005 cited in Lu et al., 2009); the figure is expected to have increased in recent times. Such a high demand in the use of alkanolamines has led to a surge in the prices of production. (BASF, 2006). Figure 2, illustrates the potential environmental fate of alkanolamines following various industrial applications.

Compound	CAS Number	Melting Point (°C)	Boiling Point (°C)	Water Solubility (mg/L)	Log P (octanol-water)	Vapor Pressure (mm Hg)	pKa Dissociation Constant	Henry's Law Constant ($atm\text{-}m^3/mole$)
MEA	141-43-5	10.5	171	1×10^6	-1.31	0.404	9.5	3.25×10^{-8}
DEA	111-42-2	28	268.8	1×10^6	-1.43	2.8×10^{-4}	8.96	3.87×10^{-11}
TEA	102-71-6	149.2	335.4	1×10^6	-1.00	3.59×10^{-6}	7.76	7.05×10^{-13}
MDEA	105-59-9	-21	247	1×10^6	-1.50	2.00×10^{-4}	8.52	3.14×10^{-11}
DIPA	110-97-4	44.5	250	8.7×10^5	-0.82	1.25×10^{-4}	9.1	6.91×10^{-11}

Table 2. Physical and chemical properties of some selected alkanolamines (Modified: Headley et al., 2002).

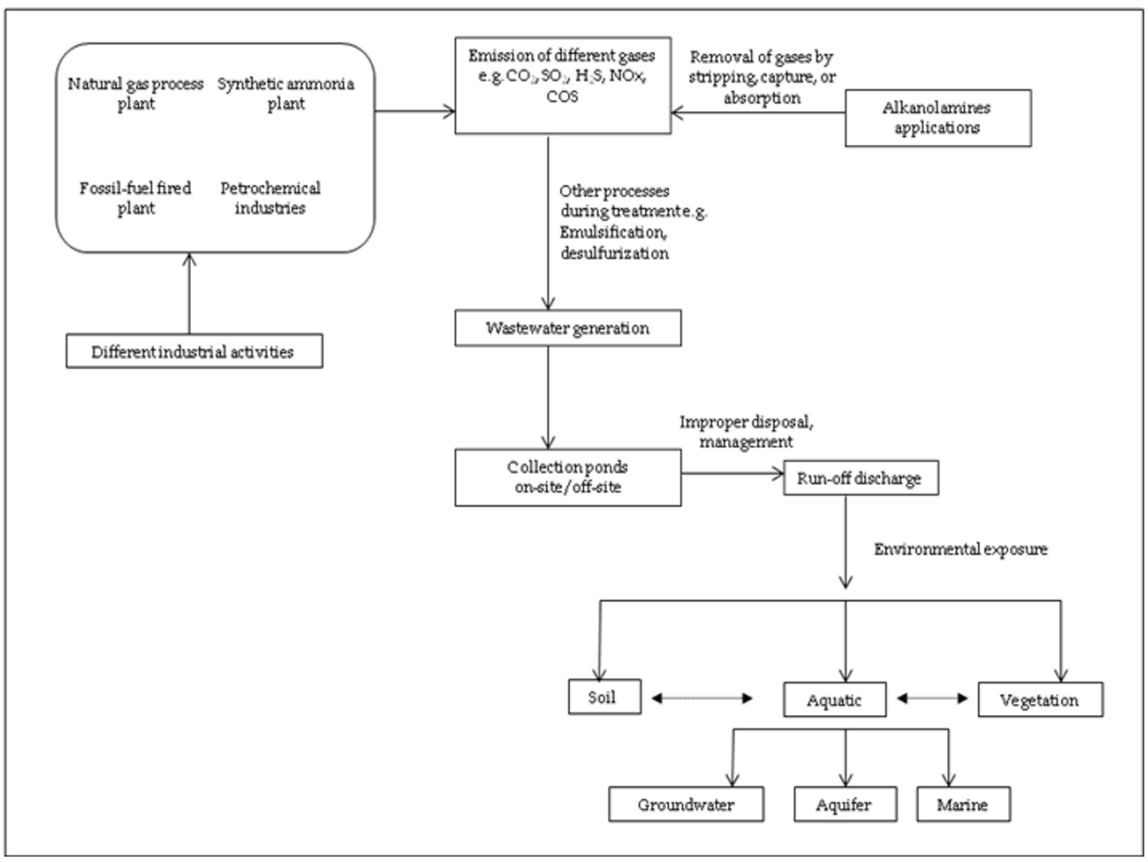

Fig. 2. Potential environmental distribution of alkanolamines.

Improper desulfurization processes results in a corrosive plant installations creating technological malfunction in transporting generated wastewater from the treatment plants. The wastewater not only composed of lyes, rinse water and column refluxes, but also process amines and their degradation products, including ammonium ion (Chackma and Meisen, 1997; Rooney and Bacon, 1998; Rooney and Bacon, 1996; 1997, as cited in Kaminski et al., 2002). One of the most commonly used alkanolamines, diethanolamine (DEA), is miscible in water due to its small molecular weight (mw 106) and high polarity (Headley et al., 2002). Such physicochemical properties mean DEA and related compounds have the potential for rapid and widespread transport in the environment and exposure to organisms. However, the concentrations of alkanolamines in natural waters are expected to be low because of dispersion processes (Hansen et al., 2010). For instance, Greene et al., (1999) (as cited in Hansen et al., 2010), reported that concentrations of the alkanolamine diisopropanolamine (DIPA) were 350 mg/L in groundwater near the source of contamination at a sour gas plant. The concentration decreased to less than 50µg/L down-gradient from the plume.

5. Methods for ionization of alkanolamines in environmental samples

5.1 Electrospray ionization (ESI)

ESI sources for use with mass spectrometers were introduced by Fenn and co-workers in 1988 (Yamashita and Fenn, 1984; Fenn et al., 1989 as cited in Rodrigues et al., 2008). Electrospray allows desorption of large, non-volatile intact analytes directly from solution. Generally, an electrospray is produced by spraying a sample solution through a capillary into a strong electric field in the presence of a flow of nitrogen, transferring the ions into the gas phase As a result of the applied electric field, the surface of the liquid emerging from the capillary is highly charged and assumes a conical shape known as the Taylor cone. When the Rayleigh limit is reached (namely the point at which the surface tension of the liquid is exceeded by the repulsive forces between the charges) the surface of the cone breaks into droplets that further fragment into smaller and smaller drops, eventually producing ions in the gas phase (Kebarle and Tang, 1993 as cited Rodrigues et al., 2008). The ESI source is easy to use, has a wide polarity range and can be applied to thermally labile compounds (Mallet et al., 2004 as cited in Raffi et al., 2009).

5.2 Atmospheric pressure chemical ionization (APCI)

APCI was originally developed as an analytical technique for analysis of trace components in the gas phase. APCI is only possible when the analyte exists in the gaseous state as ions. Since the instrument of separation for example, liquid chromatography (LC), high pressure liquid chromatography (HPLC) or GC is coupled to the MS, it is necessary to volatilize the molecules from the eluent. In APCI, the analyte is sprayed by a heated pneumatic nebulizer probe at atmospheric pressure for nebulization and a high voltage needle produces a corona discharge for ionization of the evaporated solvent. This dissociates the analyte molecule and generates ion (Raffi et al., 2009). Figure 3 gives an overview of tandem mass spectrometry operation.

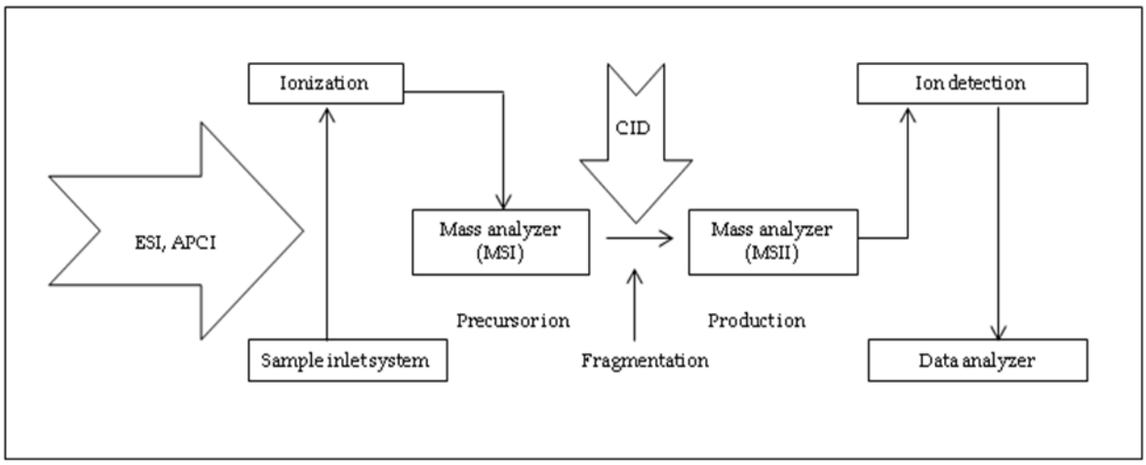

Fig. 3. Diagramatic representation of tandem mass spectrometry [Modified: Rodrigues et al., (2008)].

6. Mass analyzers for tandem MS analyzes of alkanolamines

The instrumentation used for tandem mass spectrometry of alkanolamines can be divided into three main types namely ion-trapping (quadrupole ion trap (QIT); triple quadrupoles and sector or time-of-flight instruments respectively (Payne and Glish, 2005,). The notable characteristic that differentiate ion-trapping instrumentation from other types of mass spectrometers (MSs) is that tandem mass spectrometry (MS-MS) is performed through a tandem-in-time method, instead of tandem in space. This implies that each stage of mass spectrometry is conducted in succession in the same analyzer in time. A triple quadrupole (QqQ) by contrast has each step of MS-MS operated in different analyzer separated in succession in space, i.e. an analyzer for each level of MS-MS operation (Payne and Glish, 2005). In sector instruments, each subsequent level requires the addition of another reaction region and mass analyzer. An immediately apparent advantage of trapping instruments is that multiple stages of MS-MS (MSn) can be performed without instrumental modifications. The ion intensity is the only limitation to the number of MS-MS levels possible in a trapping instrument (Louris et al., 1990 as cited in Payne and Glish, 2005). In addition, 80-90% of MS-MS product ions can be trapped unlike in linear quadrupole (LQq) where efficiencies are generally an order of magnitude lower (Johnson et al., 1990 as cited in Payne and Glish, 2005).

As much of the tandem MS applications of alkanolamines were conducted by use of triple quadrupoles, a brief discussion of these analyzers will now be given. Quadrupole mass analyzers are of two types (1) linear quadrupole and Triple quadrupole mass analyzer. By design triple-quadrupole mass spectrometers consist of two resolving quadrupoles (Q1 and Q3), and a collision cell (Q2) positioned in-between (Rodrigues et al., 2008). Triple-quadrupole mass spectrometers can be operated in four modes of acquisition: multiple-reaction monitoring (MRM), product-ion scan, precursor-ion scan, and neutral loss. MRM is the most common type of acquisition utilized for quantitative analysis. Collision induced dissociation (CID) on different brands of triple-quadrupole mass spectrometers typically results in similar fragment patterns, while significant differences may be observed in the relative abundances of the fragment ions, mainly due to the differences in instrumental design. The reason for the high sensitivity of the MRM acquisition is that the mass analyzer is monitoring the same mass to charge ratios during the entire time of the data acquisition, and the specificity is based on monitoring molecular weight and compound-specific fragmentation (Rodrigues et al., 2008; Payne and Glish, 2005).

7. Analysis of alkanolamines from environmental samples

A summary of work reported on analysis of alkanolamines in the last two decades is presented in Table 3. This table was extracted from Science Direct to identify existing peer reviewed literature published (Peters, 2011), from 1991-2011. Interestingly, only 6% of the total hits (206) of the original research had a connection with alkanolamines in relation to ecotoxicity, toxicity, biodegradation assays. Most work involved the fortification (Peru et al., 2004) or spiking, dosing of the samples with alkanolamines before the testing procedure. For each of the study, different instrumental operations were carried out to quantify (the fortified concentrations) of the test compounds (alkanolamines). It is worth mentioning that some guidelines have been established for some alkanolamines in water, soil and plants (Appendix 1). However, vis-à-vis tandem mass spectrometry, more attention will be given on the work by Peru et al., (2004) where alkanolamines were determined in cattails (*Typha latifolia*) utilizing ESI with selected reaction monitoring and ion-exchange chromatography (IEC).

Title	Subject	Environmental samples	Alkanolamines	Instrumentation	References
Seawater ecotoxicity of monoethanolamine, diethanolamine and triethanolamine	Ecotoxicity	Aquatic species: alga, oyster, mussel, crustacea	MEA, DEA, TEA	Compact Ion Chromatography (CCI)	Libralato et al., 2010
Molecular effects of diethanolamine exposure on *Calanus finmarchicus* (Crustacea: Copepoda)	Toxicity	Aquatic species: *Calamus finamarchicus*	MEA, DEA	High resolution magic angle spinning, nuclear magnetic resonance (HR-MAS- NMR)	Hansen et al., 2010
Gas chromatographic-mass spectrometric determination of sulfonane in wetland vegetation exposed to sour gas-contaminated groundwater	Plant Uptake	Wetland vegetation: roots, shoots, berries, leaves, seeds, grasses,	Sulfolane containing DIPA	Gas chromatography mass spectrometry (GC-MS)	Headley et al., 1999
Absorption, distribution, metabolism and excretion of intravenously and dermally administered triethanolamine in mice	Toxicity	Urine, feces, blood, kidney	MEA, DEA, TEA	GC-MS, LC-MS	Stott et al., 2000
Evaporation and air-stripping to assess and reduce ethanolamines toxicity in oily wasterwater	Toxicity	Wastewater	MEA, DEA, TEA	Ion chromatography system (ICS)	Libralato et al., 2008
Environmental impact of amines	Bio-degradation	Marine using alga Skeletonema costatum	8 amines including MEA, DEA, TEA e.t.c.	Organization for economic cooperation and development (OECD) guidelines 306	Eide-Haugmon et al., 2009
Investigation of the formation of N-nitrosodiethanolamine in B6C3F1 mice following topical administration of triethanolamine	Toxicity	Blood and urine	DEA, TEA	GC-MS	Saghir et al., 2005
Degradation of MMEA at absorber and stripper conditions	De-gradation	Different experimental conditions	MMEA	LC-MS; GC-MS	epaumier et al., 2011
The pharmacokinetics of diethanolamine in Sprague-Dawley rats following intravenous administration	Toxicity	Blood, liver, kidneys, heart, brain, carcass	DEA	GC-MS	Mendrala et al., 2001
In vitro human skin penetration of diethanolamine	Toxicity	Human skin	[^{14}C]-DEA*	Liquid scintillation spectroscopy (LSC)	Kraeling et al., 2004
Evaluation of the genotoxic potential of alkylalkanolamines	Genotoxicity	Blood of mice	DMEA, MDEA, t-BDEA	Biological assays	Leung and Ballantyne, 1997
The inhalation of di- and triethanolamine upon repeated exposure	Toxicity Viscera of mice	Liver, kidneys, brain, lungs of mice	DEA, TEA	Gravimetric determination	Gamer et al., 2008

Table 3. Instrumentation used in analyzes of alkanolamines from environmental matrices.

For tandem mass spectrometry of alkanolamines from environmental samples, certain procedures must be adhered to for maximum level of detection and high quality data generation. The key steps include: extraction of the compound of interest from the matrix of containment, cleanup of the extract to reduce interference by other co-exiting compounds, pre-concentration to reduce the solvent of extraction hence increase the sensitivity and therefore the detectability of the analyte by instrumental analysis, and finally the actual determination to quantify the precise amount or concentration of the compounds in the original sample. A thorough outline of the sampling site, how much sample, and the representativeness of the sample for statistical analysis must be thought through before the sampling operations.

The application by Peru et al., (2004) will now be discussed as an example of tandem MS for the detection of alkanolamines in environmental samples. The method employed ion chromatography separation (Peru et al., 2004). Their work documented improvements in the selectivity and detection limits of a selected reaction monitoring (SRM) method for the quantification of DIPA in vegetation tissue. They extended the sphere of the method to the determination of other related alkanolamines including MEA, DEA, MDEA, MIPA, and TEA) in the upper (shoots) and lower (roots) tissues of *Typha latifolia* (cattails) grown hydroponically with various levels of exposure to DIPA under controlled laboratory conditions (Peru et al., 2004).

8. Tandem MS for determination of alkanolamines in cattails

Doucette et al., (2002) (as cited in Peru et al., 2004), has elaborated on the sampling, fortification and laboratory growing conditions of cattails analyzed for alkanolamines. In summary, the plants were obtained as bare-root plants from the Aquatic and Wetland Company (Fort Lupton, CO, USA). Following their reception, they were transplanted into 12 separate glass reactors and grown hydroponically under aerobic conditions for several weeks prior to analysis (Peru et al., 2004).

8.1 Extraction of plants

Samples were prepared as described previously by Headley et al., (1999). Briefly, tissues were prepared and extracted using different methods where: (a) about 1g of subsample of soil soil-free plant was homogenized after thawing with organic-free Milli-Q water and (b) the ample portion of tissue sample was ground under liquid nitrogen to a free-flowing powder and then centrifuge. The sample was allowed to warm to room temperature before adding Milli-Q water to avoid ice formation in the following extraction step. In both cases, further centrifugation was carried out for 45 minutes at 2500rpm to remove large debris. The supernatant was filtered using a 0.45µm surfactant-free cellulose acetate membrane filter. Sub-samples of 500µL of the extract were taken, and 10µL of 20% formic acid were added to each to ascertain complete ionization of DIPA. TEA was used as the internal standard of final extract concentration of 0.5µg/mL. TEA was chosen as the internal standard (IS) because of its similar chemical properties to those of DIPA (Headley et al., 2004). For other matrices such as sediment or soil, the extraction of sample might require more rigorous methods as mentioned above and may require some clean up steps before direct injection or derivatization (to be discussed later) of the extract.

8.2 Calibration of standards

Standard solutions for calibration or spiking are very important in the entire analytical procedure using MS-MS technique. They must be prepared from original stock of high quality with high purity. Similarly, a suitable solvent (s) must be prepared used and water of an analytical grade and purity. The standard alkanolamines must be prepared in stock solution and the necessary dilution carried out for fortification and calibration. Acetonitrile (ACN), acetone (ACE) or a mixture of the two is commonly used as versatile solvent for chromatographic analysis of most compounds (Bu et al., 2000, Nödler et al., 2010). Again, the choice of solvent depends on the matrix from the alkanolamines are to be extracted. In the study under review, individual and mixed stock solutions of alkanolamines (1000µg/mL) were prepared and appropriate dilutions made with water: methanol (1:3 v/v) with the water containing 0.1% formic acid. All standard solutions are usually stored at 4°C. It is vital that all glassware is cleaned and rinsed with methanol, dried in the oven at 100°C to minimize contamination (Peru et al., 2004).

8.3 Instrumentation

There have been few developments in the use of LC-MS for the analysis of alkanolamines. RP-HPLC with thermospray (TSP) interface has been used to detect primary, secondary, and tertiary amines in water (Imago et al., 1993 as cited in Headley et al., 2002). The use of the soft ionization techniques such as direct insertion probe-positive ion chemical ionization (DIP-PICI) and ESI in combination with MS and tandem MS-MS for the detection and confirmation of alkanolamines in water has been reported (Dickson et al., 1996). Under soft ionization conditions, alkanolamines give intense protonated molecular-ions with little or no fragmentation (Dickson et al., 1996), which is well suited for MS-MS analyzes. Increased specificity was obtained using MS-MS as compared to MS. The benefits of MS-MS mixture analyzes include increased confidence in identification of unknowns and analyte confirmations, improved detection limits through reduction in chemical noise, and the availability of a variety of operating modes which can be used for screening, target compound analyzes, and confirmation (Harrison, 1983; Yost and Enke, 1979, as cited in Headley et al., 1999, 2002).

Among the methods available for analyzes of alkanolamines, techniques employing GC or LC with direct aqueous injections have received the most attention (Headley et al., 2002). To this end, Peru et al., (2004) conducted IEC using a Waters 2695 separations module with a Dionex IonPac CS14, 2mm x 25cm cation-exchange column to determine alkanolamines in cattail tissue. The eluent consisted of 75:25 methanol/water containing 0.1% formic acid (isocratic) with a flow rate of 200µL/min. An injection volume of 10µL was used for all samples and standards.

In Peru et al., (2004) study, a Quattro Ultima triple-quadrupole mass spectrometer (Micromass, UK) using positive ESI was used for all analyzes. For comparison, both selected ion monitoring (SIM) and selected reaction monitoring (SRM) modes were employed. For ESI-MS, instrumental parameters were as follows: source temperature 90C, cone voltage setting 26V, capillary voltage setting 1.81 kV, hexapole 1 4.0V, hexapole 2 and aperture 0V, desolvation temperature 220°C, desolvation gas N_2 flow 488L/h, cone gas N_2 flow 145L/h, and nebulizer gas N_2 flow was at maximum. Peak width was set to achieve unit mass resolution, and the multiplier was set to 650V. All analyzes were performed using ESI in the positive-ion mode. Initial quantitative analyzes used selected ion recording, monitoring $[M+H]^+$ ions at *m/z* 134 for DIPA and *m/z* 150 for TEA (IS), with an inter-channel delay of 0.10s and a dwell time of

0.50s. For ESI-MS-MS, used to provide additional selectivity, SRM was utilized as the final method of quantification. Instrumental conditions were as above for ESI-MS with the following exceptions/additions: argon was used as the collision gas at a pressure sufficient to increase the Pirani gauge reading to 3.53×10^{-4} Torr. Collision energy was set at 17V (laboratory frame of reference). Reaction monitoring was used for quantification, monitoring losses of either one or two molecules of water. Although quantification of only DIPA *(m/z* 134→98) along with TEA (*m/z* 150→132) as the internal standard) was required for this study, other relevant alkanolamines were examined to determine the applicability of the method for future investigations. Product ion scans (Figures 4a-f) were acquired to determine suitable transitions for reaction monitoring, and are listed in Table 4.

Compound	MW	Precursor ion *m/z* $[M+H]^+$	SRM transition* monitored for quantification
MEA	61	62	62>44
MIPA	75	76	76>58
DEA	105	106	106>88
MDEA	119	120	120>102
DIPA	133	134	134>98
TEA	149	150	150>132

Table 4. Transitions monitored during SRM analysis (Peru et al., 2004) * All SRM analysis completed using 18eV collision energy (Q2), argon as collision gas (cell pressure 3.53×10^{-4} Torr).

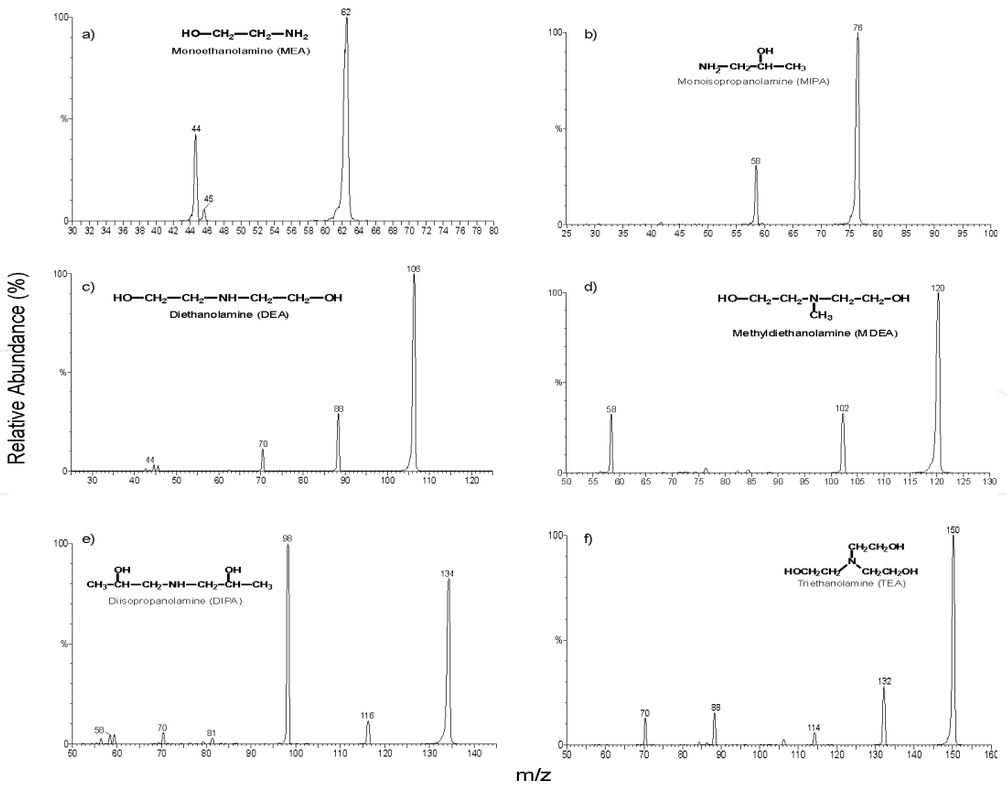

Fig. 4. Product ion spectra of $[M+H]^+$ ions of six alkanolamines (MEA, MIPA, DEA, MDEA, DIPA, TEA) (Peru et al., 2004).

As demonstrated in Figures 4 (a-f), the main product ions were formed via water loss. Typically, the loss of one or two water molecules is not considered a highly specific transition to monitor for SRM analysis. Nonetheless, in this case, there were no other options. Moreover, SRM using the loss of 2(H_2O) for DIPA and H_2O for TEA (IS) provided adequate specificity to exclude SIM interferences experienced during the study (Peru et al., 2004).

The improved sensitivity and resolution of SRM mode in the study of Peru et al., (2004) is demonstrated in Figure 5 for DIPA. In Figure 6A, approximately 10% of the samples had prohibitive mass interference that could not be resolved either chromatographically or by mass spectrometer. Product ion scans were acquired to determine whether suitable product ions were formed that could be used for MRM to improve selectivity.

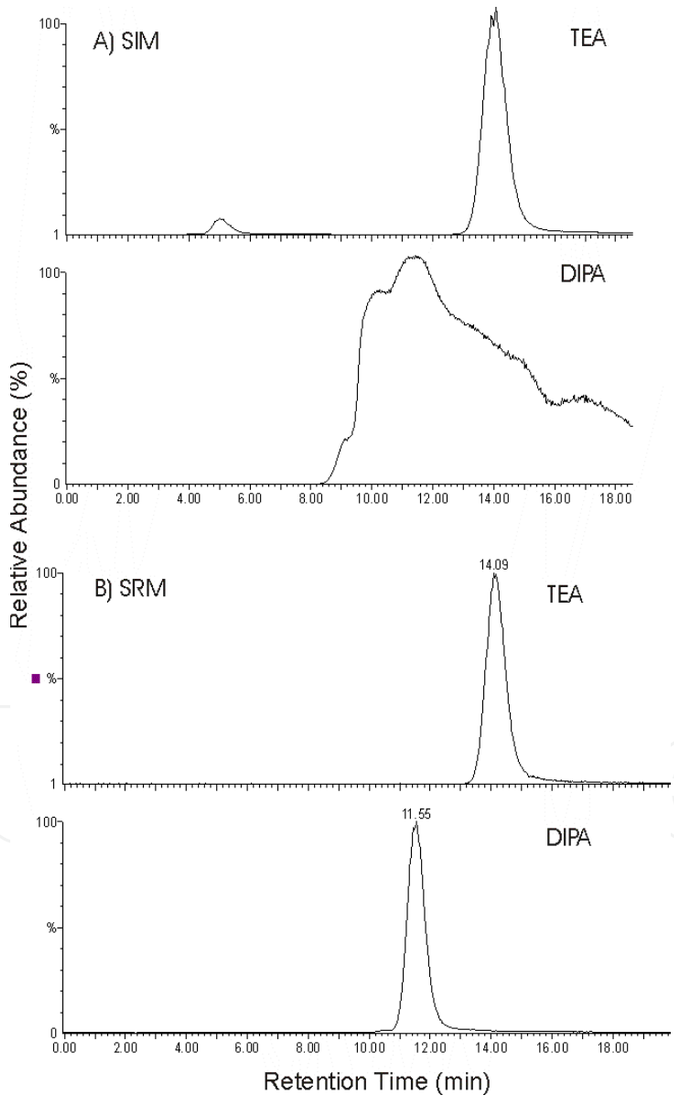

Fig. 5. (A) Selected ion monitoring chromatogram illustrating prohibitive interference during the analysis of DIPA. (B) Chromatogram of the same extract in used (A) illustrating the selectivity of MS-MS using SRM (Peru et al., 2004).

9. Overcoming matrix effect- enhancement and suppression of ions

Though LC-MS-MS is a useful analytical characterization tool, there is one significant setback of electrospray mass spectrometry. This is its high susceptibility to matrix signal suppression or enhancement which is a major challenge for quantitative LC-MS application of environmental samples (Choi et al., 2001). Matrix effects occur when molecules coeluting with the compound/s of interest alter the ionization efficiency of the electrospray interface. The exact mechanism of matrix effects is unknown, but it probably originates from the competition between an analyte and the coeluting, undetected matrix components (Taylor, 2005). King et al., (2000) (as cited in Taylor, 2005) have shown through a series of experiments that matrix effects are the result of competition between nonvolatile matrix components and analyte ions for access to the droplet surface for transfer to the gas phase. They conclude that the exact mechanism of the alteration of analyte release into the gas phase by these nonvolatile components is unclear. They postulate a likely list of effects relating to the attractive force holding the drop together and keeping smaller droplets from forming should account for a large proportion of the ionization suppression observed with electrospray ionization. Depending on the environment in which the ionization and ion evaporation processes take place, this competition may effectively decrease (commonly known as ion suppression) or increase (ion enhancement) the efficiency of formation of the desired analyte ions present at the same concentrations in the interface. Thus the efficiency of analyte ions to form is very much dependent on the matrix entering the electrospray ion source (Taylor, 2005). However, King et al. (2000) (as cited in Taylor et al., 2005) have demonstrated that ion suppression is much more severe with ESI than APCI. The increased ion suppression is a result of high concentrations of nonvolatile materials present in the spray with the analyte. Another reason for the higher ion suppression in the ESI mode could be due to the fact that in this mode, unlike in the APCI mode, the analyte is ionized in the liquid phase inside the electrically charged droplets. As the solvent evaporates, the analyte precipitates from solution either as solid compound or as a co-precipitate with other non-volatile sample components (Raffi et al., 2009).The two main techniques used to determine the degree of matrix effects on an ESI–MS-MS method are: (1) post-extraction addition which is considered to be a static technique providing information about matrix effect at the point of elution of the analyte, and (2) post-column infusion, a more dynamic technique involving an infusion pump that delivers a constant flow of analyte into the LC effluent at a point after the chromatographic column and before the mass spectrometer ionization source (Taylor, 2005).

Different plan of action can be employed to overcome matrix effects during tandem mass spectrometry. These include but not limited to: (a) modification of the sample extraction procedure and (b) improved chromatographic separation (Avery, 2003 as cited in Taylor, 2005). In addition, the application of internal standards has been especially useful in addressing quantitative signal reproducibility issues between standard and matrix analytes (Boyd, 1993; Temesi, 1999 as cited in Choi et al., 2001). In order to determine if there were matrix effects during the analysis of alkanolamines in their study, Peru et al., (2004) utilized the post-column technique as illustrated in Figure 6.

9.1 Post infusion technique for alkanolamines determination in cattails

A mixture of the alkanolamines at a concentration of 1µg/mL, for each component was infused post column at a rate of 25µL/min. This gave rise to an elevated baseline. Blank extracted cattail root matrix was then injected via the LC system and the multiple reaction monitoring transitions (Table 4) were monitored (Figure 7). If ionization enhancement or

suppression exists, a positive or negative deflection in the elevated baseline would be observed. As shown in Figure 8, some suppression was observed (symbolized with an *) prior to the retention times of the analytes of interest. These results indicated that suppression/enhancement matrix effects were not significant for the analytes investigated.

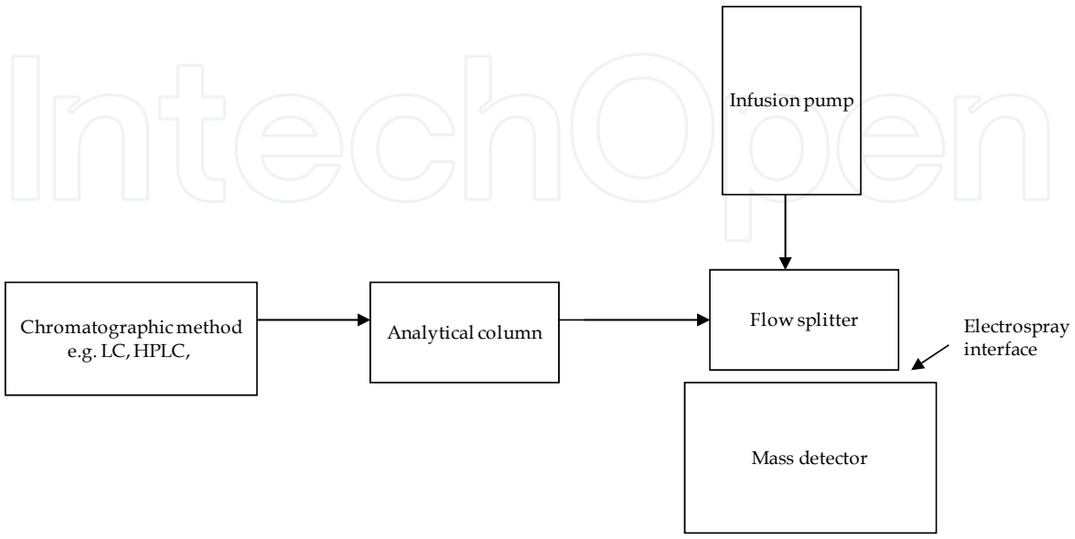

Fig. 6. Schematic of post-column infusion system [Modified from Taylor, (2005)].

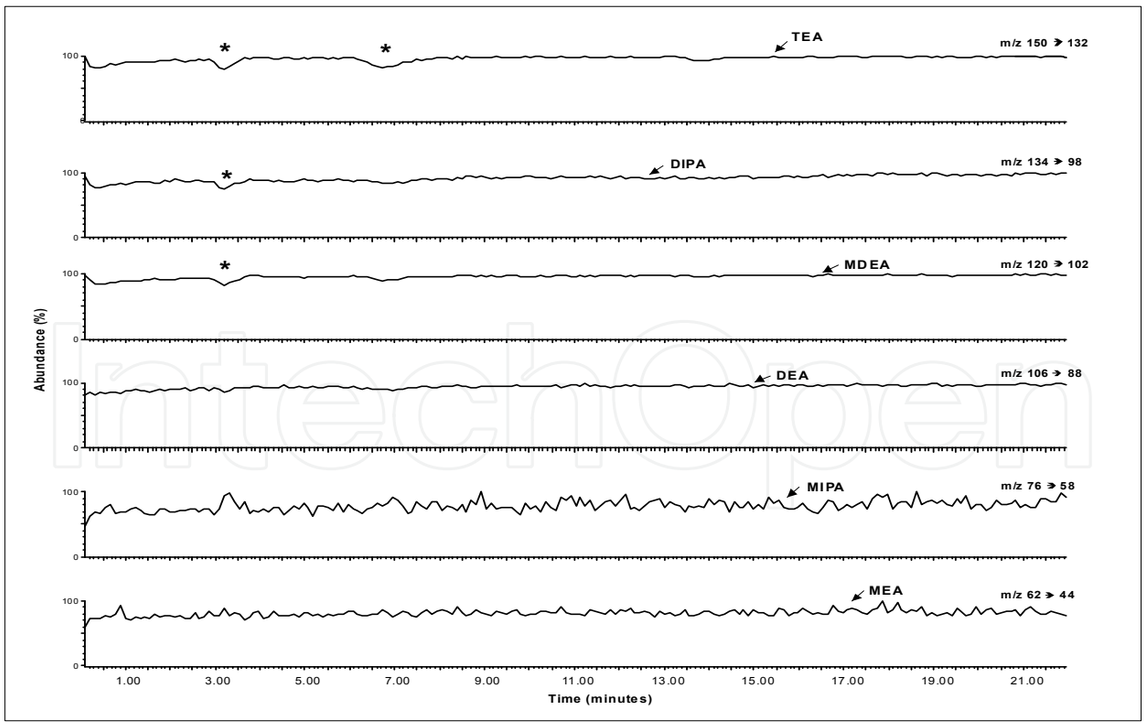

Fig. 7. Multiple reaction monitoring chromatogram (transitions monitored as per Table 4) of a mixture of six alkanolamines post column infusion to ascertain ionization enhancement/suppression (Peru et al., 2004).

Improved chromatographic separation was achieved using a Dionex CS14 cation-exchange column for reliable quantification of the selected alkanolamines (Figure 8). Chromatography and instrumental sensitivity did not decline significantly during the course of analyzes (over 80 vegetation extractions analyzed during a 3-week duration), while evaluation of between-day precision based on replicate samples gave a RSD values of <10% indicating an overall method robustness (Peru et al., 2004).

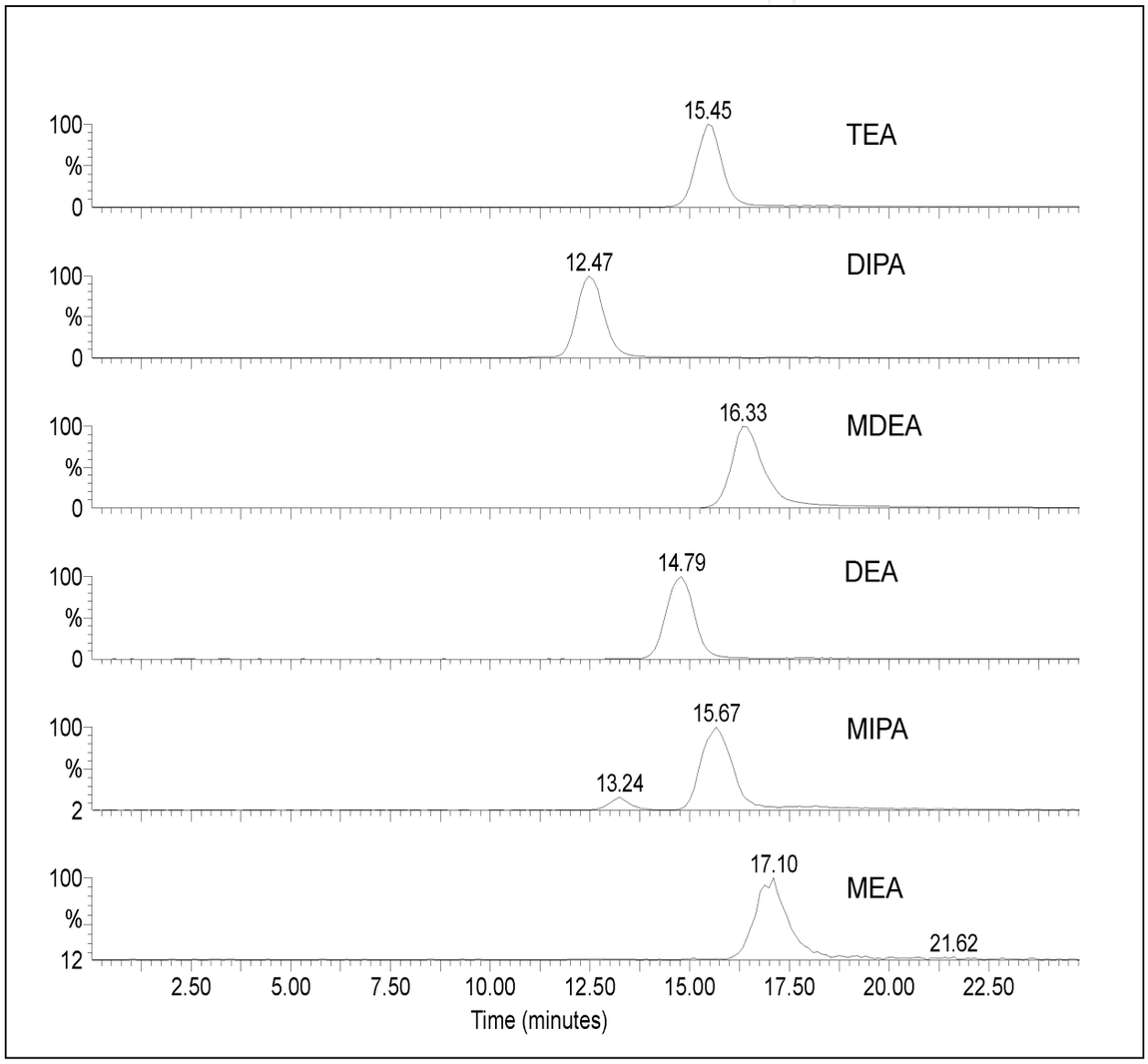

Fig. 8. Improved chromatographic separation of six alkanolamines using ion-exchange chromatography and MRM (transitions monitored as per Table 4) (Peru et al., 2004).

9.3 Quantification calculation of alkanolamines in cattails

Signal to noise ratio (S/N) is one of the most important performance characteristics considered in assessment to measure low analyte levels in environmental samples. In routine practice, the S/N value is used for prediction of LOQ (Kovalczuk et al., 2006).

Instrumental detection limits (DL), based on three times the signal-to-noise (S/N) ratio obtained from spiked blank matrix extract, improved using SRM for three of the five alkanolamines previously reported using SIM; DIPA 6 pg vs. 20 pg, TEA 4 pg vs. 30 pg and MDEA 14 pg vs. 32 pg injected. MEA and DEA provided poorer detection limits as compared with those previously reported; MEA 300 pg vs. 40 pg and DEA 47 pg vs. 40 pg injected. MIPA was not included in the SIM method therefore its DL of 104pg injected could not be compared. Likewise, limit of quantification (LOQs) for DIPA (2.6ng/g), TEA (5.2ng/g) and MDEA (18.6ng/g) represented were an improvement on the reported value of 20ng/g for each alkanolamine obtained using the SIM method. For both MEA (200 ng/g) and DEA (6 ng/g), sensitivity was compromised for selectivity. MIPA gave a LOQ of 69 ng/g. LOQs were calculated using an S/N ratio of 6:1 from data obtained for extracts of spiked root matrix. At this S/N ratio, variability in the reported LOQs was <10%relative standard deviation (RSD). The linearity for calibration standards, ranging from 0.01–1.00mg/mL, had r^2 values ranging from 0.9966–0.9999. For all the alkanolamines investigated, the response began to plateau (deviate from linearity) at concentrations above 3.00 mg/mL. Blank root tissues were spiked at two levels based on upper and lower levels expected in samples (2.5 and 10µg/g). Recoveries ranged from 76–116% for the 2.5mg/g level and 68–98% for the 10mg/g level with RSD <10%, n=6 (Table 5) (Peru et al., 2004).

Alkanolamines	Recovery (%) in root matrix ±SD (2.5µg/g)	RSD (%) (n=6)	Recovery (%) in root matrix ±SD (10.0µg/g)	RSD (%) (n=6)
TEA	92±1.1	4.4	83±3.2	3.9
DIPA	76±1.3	5.2	77±6.1	7.9
MDEA	106±2.4	6.0	98±3.5	3.6
DEA	77±1.2	3.6	68±3.6	5.3
MIPA	84±2.6	8.1	84±6.7	7.9
MEA	116±2.3	7.6	94±7.4	7.8

Table 5. Recovery data of six alkanolamines from fortified *Typha latifolia* root (fortification concentration in parenthesis) (Peru et al., 2004).

9.4 Derivatization of alkanolamines

To date, there are a few methods and techniques that use derivatization steps to improve the detectability of alkanolamines from environmental samples. These protocols however, do not use tandem mass spectrometry for quantification. They involve GC-MS, LC, and /or IEC as separation tool to mobilize the analytes from the matrices. The detection, confirmation and quantification of alkanolamines either use fluorescence or conductivity techniques (Serbin and Birkholz, 1995 as cited in Headley et al., 2002).

10. Conclusions

According to Headley, et al., (2002), the choice of which procedure is adopted in a given laboratory, for the determination of alkanolamines will be based primarily on the expertise and instrumentation available in such laboratory. Where appropriate, methods employing direct aqueous injections of samples are best suited for analyzes of alkanolamines in environmental samples. These methods eliminate the time and expense of organic solvent extraction procedures. While capillary GC columns have also been used for the analysis of the alkanolamines, best results have been achieved using LC methods with or without derivatization steps. Because procedures employing advances in positive-ion electrospray ionization techniques with IC- MS-MS detection have proven useful for the confirmation and recovery of alkanolamines in wetland vegetation such as cattails, it is of essence that future research should focus on the determination of the native compounds from different samples from the environment. Further developments will likely centre on mass spectrometric analyzes for identification of metabolites and transformation products in aquatic environments. Such work would assist in policy making to control the level of discharge of these compounds into the environment.

11. Appendix 1

11.1 Guidelines for some common alkanolamines in water, soil and plants

Though the preceding section enumerated studies carried out by different academic research groups on alkanolamines, it should be mentioned that some governmental projects have been carried out in Canada by different agencies such as the Canadian Council of Ministers of the Environment (CCME), the Canadian Association of Petroleum Producers (CAPP) and Alberta Environment (AENV) to set guidelines for the levels of alkanolamines that are allowed into environmental compartments (water, soil and plant/vegetation) from discharges generated by chemical industries where green house gases are emitted and the application of alkanolamines are required. These guidelines originated basically by collating different research works that have been carried out on alkanolamines and limits were set based on a wide range of data collected from toxicological, ecotoxological and genotoxicological studies.

Reports on the presence of anthropogenic DIPA in the environment are limited to data collected at sour gas processing facilities in western Canada (CAPP 1997; Wrubleski and Drury 1997 as cited in CCME, 2005). The maximum measured DIPA concentration in groundwater was 590mg/L in a shallow till aquifer (Greene et al. 1999 as cited in CCME, 2005). No studies were found that had detected DIPA as a naturally occurring compound in the environment (CCME, 2005).

Uptake of DIPA by wetland vegetation was studied as part of a research program to evaluate natural attenuation processes in contaminated wetlands (CAPP 1998, 1999, 2000 as cited in CCME 2005). Roots, stems, leaves, flower heads, seed heads, and berries of cattail, dogwood, sedge, marsh reed grass, cow parsnip, and smooth brome growing in a DIPA impacted wetland were included in the study (CAPP 1999, 2000; Headley et al. 1999a,b as cited in CCME, 2005). Analytical results indicated highly variable DIPA concentrations for different parts of the same species (e.g., roots versus leaves), between different plant species (e.g., cattail leaves versus sedge leaves), and even between different samples of the same

part of the same species. Although the maximum measured DIPA concentration in water in the wetland was only 13mg/L, DIPA concentration as high as 208mg/kg were measured in the plants (CCME, 2005).

Environmental sample	Alkanolamines	Guide line values (mg/L)
Aquatic		
Fresh water	DIPA*	1.6[a]
Marine		NRG
Human drinking water	DEA	0.06
	MEA	0.6
Fresh water aquatic life	DEA	0.45
	MEA	0.075
Agricultural Soil		Guideline values (mg/kg)
Fine soil	DEA	2.0
	MEA	20
Coarse soil	DEA	3.5
	MEA	10

Table 6. Guidelines values for some common alkanolamines (Collated from CCME, 2005 and Government of Alberta, 2010). *Data sourced from CCME, 2005. [a]Interim guideline; [b]No recommended guideline.

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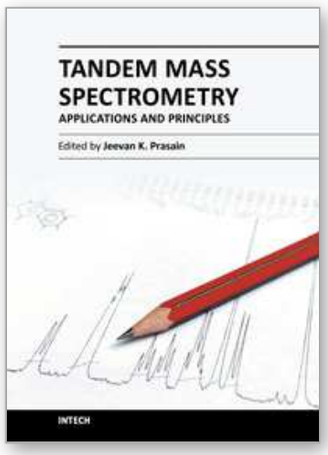

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