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# Review of separation methods for the determination of ammonium/ammonia in natural water

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A B S T R A C T

Ammonium ($NH_4^+$) and ammonia ($NH_3$) in aquatic ecosystems are of great interest to environmental scientists because they can be used to study the nitrogen cycle and as water quality indicators. Analytical separation methods developed in recent decades have been used widely to determine $NH_4^+$ and $NH_3$ in aqueous solutions. This review presents an overview of state-of-the-art separation methods and analytical techniques for determining $NH_3/NH_4^+$ in natural water, including chromatographic methods, electrophoretic methods, extraction methods, membrane-based gas diffusion methods, membraneless gas diffusion methods, passive sampling methods, and paper-based analytical methods. Common detection techniques that can be used in conjunction with particular separation methods are described, phase-transfer strategies (liquid-liquid, liquid-solid, liquid-membrane-liquid, and liquid-gas-liquid methods) are highlighted, and the strengths and weaknesses of the separation methods are discussed. The outlook, challenges, and expected future developments in the field of separation methods for determining $NH_4^+$ and $NH_3$ in natural water are presented.

## 1. Introduction

Determining ammonium ($NH_4^+$) and ammonia ($NH_3$) concentrations to allow the spatial distributions of $NH_4^+$ and $NH_3$ in aquatic ecosystems to be studied is important to environmental scientists. Information obtained by analyzing $NH_4^+/NH_3$ can be used to evaluate the environmental quality of an aquatic ecosystem and to study the nitrogen biogeochemical cycle [1]. Large temporal and spatial $NH_4^+/NH_3$ datasets could facilitate aquatic ecosystem protection, high quality drinking water supplies, and water quality trend predictions [2,3].

$NH_3$ and the positively charged form $NH_4^+$ are the most reduced natural nitrogen species. The pH of water controls the $NH_4^+/NH_3$ ratio. The $NH_3$ fractions ($\delta_{NH3}$) and $NH_4^+$ fractions ($\delta_{NH4}$) at equilibrium at different pH values are shown in Fig. 1. Unpolluted seawater is generally at pH 7.5–8.4 [4], but freshwater generally has a wider pH range. The US Environmental Protection Agency has published an aquatic life criterion of pH 6.5–9 [5]. $NH_4^+$ (pKa 9.25 at 25 °C) is dominant in most natural water, so $NH_4^+$ is generally used here to mean total $NH_4^+$ and $NH_3$ in water.

$NH_4^+$ concentrations in natural water can vary over several orders of magnitude, from several to hundreds of nanomoles per liter. $NH_4^+$ in surface water is transformed into other forms of nitrogen through biological and chemical processes. $NH_4^+$ is an important source of nitrogen for aquatic organisms [1,6]. $NH_4^+$ concentrations in unpolluted surface water can reach several millimoles per liter [7]. In some cases (e.g., in the open ocean), $NH_4^+$ concentrations in water are as low as several nanomoles per liter [8,9]. $NH_4^+$ concentrations are often high (up to several hundred millimoles per liter) in municipal and industrial wastewater [10]. It is difficult to determine a wide range of $NH_4^+$ concentrations in water using a single method, so multiple approaches are generally used.

Typical methods that are used to separate $NH_4^+$ and $NH_3$ from matrix components are shown in Fig. 1. $NH_4^+$ is dominant at low pH values and can be separated from matrix components using ion-exchange methods. However, $NH_3$, which is volatile and can diffuse from the sample, is dominant at high pH values. Typical separation methods that are used to determine $NH_4^+$ are shown in detail in Fig. 2. The methods can be divided into three types, (1) direct measurement methods using ion chromatography (IC) or capillary electrophoresis, (2) methods in which $NH_4^+$ is derivatized to give a larger molecule that strongly absorbs UV/visible light or emits fluoresces and is extracted from the sample before being determined by UV/visible or fluorescence spectroscopy, and (3)

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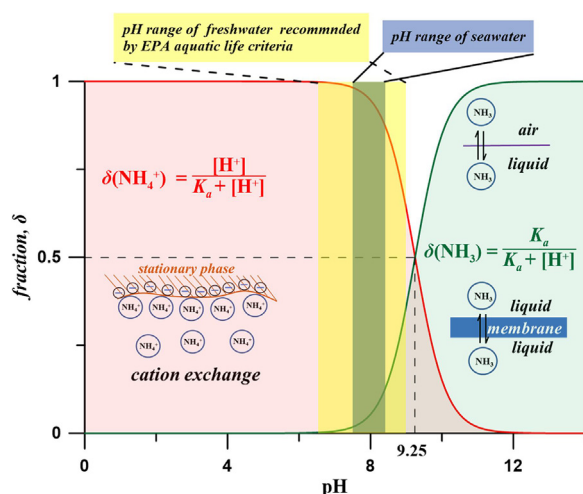  *E-mail address:* liangyi0774@guet.edu.cn (Y. Liang).

**Fig. 1.** Fractions of $NH_4^+$ species as a function for pH and typical separation pathways for the determination.
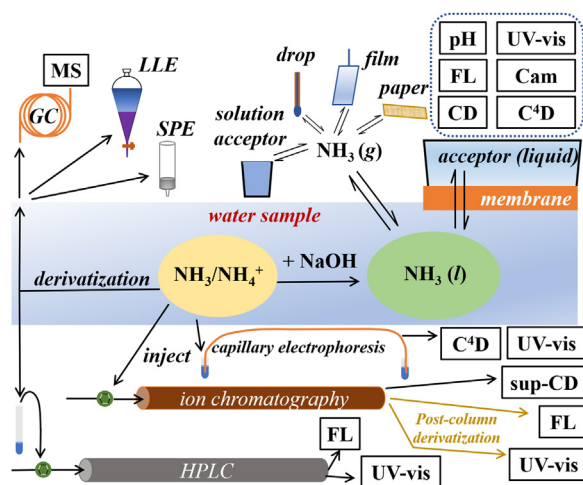


**Fig. 2.** Overview of the typical separation methods for the determination of $NH_4^+$ and $NH_3$. A square frame indicates a detection method: pH, pH meter; UV–vis, UV–vis spectrophotometry; FL, fluorometry; Cam, digital camera; CD, conductometry; $C^4D$, capactively copuled contactless conductivity detection; sup-CD, suppressed ion chromatography and conductivity detection; MS, mass spectrometry. GC, gas chromatography; HPLC, high performance liquid chromatography; LLE, liquid-liquid extraction; SPE, solid phase extraction.

methods in which $NH_3$ is diffused into the gas phase or through a membrane and then trapped and detected.

Methods that are often used to determine $NH_4^+$ and $NH_3$ are also shown in Fig. 2. Conductometry, which is used after IC, requires a suppressor to be used before the detector to decrease background conductance. A method called contactless conductivity detection or capacitively coupled contactless conductivity detection ($C^4D$) is often used with capillary electrophoresis. In this method, the electrodes are not in contact with the solution. This avoids the electrodes corroding and the results being affected by the high voltages used. UV/visible spectrometry (UV–vis), fluorometry, conductometry, pH meters, and even digital cameras on mobile phones have been used with non-chromatographic separation methods. The detection methods are discussed in more detail below.

Determining $NH_4^+$ in water after using a separation method offers many advantages over determining $NH_4^+$ in water without using a separation method. Some advantages are described here.

(1) Other ionic compounds can be determined at the same time as $NH_4^+$ to give a more complete understanding of the sample. (2) Chromatographic separation allows $NH_4^+$ to be determined separately from other amine compounds, which is difficult to achieve using non-chromatographic methods. (3) Converting $NH_4^+$ into $NH_3$ and then transferring the $NH_3$ to another phase allows interferences from other compounds to be eliminated, meaning simple universal detection methods such as a pH meter or conductometry can be used. This makes it possible to make the method portable for field use. (4) Phase separation or extraction involves enrichment, which means the method will be sensitive. (5) Separation and enrichment are key processes allowing nitrogen stable isotopes in $NH_4^+$ to be studied [11].

Several reviews of $NH_4^+$ analysis methods have been published in the last 15 y. In 2006, Molins-Legua et al. [12] compared several methods for determining $NH_4^+$ in water. In 2014, Šraj et al. [8] published an overview of flow-based methods for determining $NH_3$ in estuarine and marine water. Ma et al. [9] summarized and discussed methods for determining $NH_4^+$ at nanomolar concentrations in seawater. In 2017, Krishnan et al. [13] assessed biosensor approaches for determining exhaled $NH_3$. Kwak et al. [14] recently reviewed techniques for determining $NH_3$ in the gas phase. Other reviews have been published focused on methods for determining $NH_4^+$ using ion-selective membrane electrodes for *in situ* environmental analysis [15] and electronic sensors for determining nutrients [16]. When this paper was being prepared, three reviews of $NH_4^+$ analysis methods have been published. Zhu et al. [17] focused on methods for seawater. Lin et al. [18] discussed progress between 2014 and mid-2019. Li et al. [19] reviewed methods for determining $NH_4^+$-N in water, including optical detection, electrochemical detection, and biological enzyme detection methods. To the best of our knowledge, separation methods used when determining $NH_4^+$ in water have not previously been reviewed. Here, a wide range of separation methods used when determining $NH_4^+$ in environmental water samples are reviewed. Progress in relevant analytical methods over the last 5 y are also discussed.

## 2. Chromatographic and electrophoretic methods

It is not common to separate $NH_4^+$ from matrix components by reversed-phase high-performance liquid chromatography (HPLC) or gas chromatography (GC) because optical detectors used with HPLC and mass spectrometers used with GC are not sensitive enough to determine underivatized $NH_4^+$ in water samples. Therefore, a derivatization step is often used to convert $NH_4^+$ into a form suitable for analysis by HPLC or GC. In HPLC methods, $NH_4^+$ is normally derivatized with *o*-phthalaldehyde (OPA) to give an intensely fluorescent isoindole [20,21]. In GC mass spectrometry methods, an alkyl chloroformate (e.g., butyl chloroformate) is used to convert $NH_4^+$ into a higher molecular mass derivative [22–24]. Sometimes, derivatization is followed by solid-phase micro-extraction to make GC analysis more sensitive [23,24]. Derivatization improves the sensitivity but makes water analysis complicated, so is not generally applicable.

### 2.1. Ion chromatography

An advantage of determining $NH_4^+$ by IC is that other amines in a sample can be determined separately but simultaneously. In IC, $NH_4^+$ is separated either through ion exchange or ion exclusion [25], but most commonly through ion exchange [26]. $NH_4^+$ can be separated from alkali and alkaline earth cations more effectively using modified cation-exchange resins or new materials than using common resins [27–29]. Suppressed conductivity [30] and non-suppressed conductivity [31] conductometry methods have been

used. In suppressed conductivity conductometry, the suppressor partly converts $NH_4^+$ into $NH_3$, giving a non-linear response [32] that may require a polynomial fitting curve. High sensitivity or simultaneous determination of all inorganic nitrogen species can be achieved using post-column derivatization [33–35] and indirect detection [36].

$NH_4^+$ is retained in a very similar way to $Na^+$ by cation-exchange columns. $Na^+$ is a major ion in natural water, and the $Na^+$ concentration can be hundreds to thousands of times higher than the $NH_4^+$ concentration. $Na^+$ can therefore strongly interfere with $NH_4^+$ in most chromatographic separations. The ability of IC to handle high-ionic-strength samples can be improved by using a high-capacity ion-exchange column [37], adding an 18-crown-6 ether into the eluent [38], using a new resin containing a crown ether group [39,40], or using the column switching approach [41,42]. $NH_4^+$ and amines in saline water can effectively be determined by introducing an additional separation step, such as a purge-and-trap step [43] or gas-diffusion step [44,45], before sample injection. In 2017, Ferreira et al. [46] extracted $NH_4^+$ and low-molecular-mass amines from saline water using an ultra-sound-assisted purge-and-trap device before performing IC. The method tolerated $Na^+$ and $K^+$ concentrations up to 56,000 and 24,000 times. In 2016, researchers in the same group proposed that $NH_4^+$ and amines could be separated from a sample by steam distillation [47].

Kurzyca et al. [35] used an anion-exchange column to separate $NH_4^+$ (which was not retained) from nitrite and nitrate (which were separated) in saline water. $NH_4^+$ was detected using a post-column reaction using the Nessler reagent, and nitrite and nitrate were directly detected by measuring UV absorption at ~205 nm. Liu and Yu [36] described a UV detection method for indirectly determining $NH_4^+$ in which an imidazolium ionic liquid acted as an UV absorption reagent and the IC eluent. $NH_4^+$ was separated and detected within 13 min with a limit of detection (LOD) of $0.06 \, mg \, L^{-1}$ ($3.3 \, \mu mol \, L^{-1}$).

## 2.2. Electrophoretic separation

Electrophoretic methods, including capillary and microchip electrophoresis [48,49], have been used to determine $NH_4^+$. $NH_4^+$ has been determined using almost all electrophoretic separation modes, including capillary zone electrophoresis [50], electro-chromatography [51], and isotachophoresis [52–54]. Electrophoresis-based methods give a high separation efficiency, but capillary and micro-channel electrophoresis methods are not very sensitive. $NH_4^+$ does not strongly absorb UV wavelengths >205 nm, so indirect spectrometry was used in most early studies [55–58]. $NH_3$ absorbs UV at 200 nm because an electron can be transferred from an n-orbital to a $\sigma^*$-orbital. Direct UV detection can therefore be achieved using an alkaline background electrolyte (pH 10) to convert $NH_4^+$ into $NH_3$ [59]. The difficulties involved in using absorption detection methods have led to $C^4D$ methods being used most often in recent years [60]. $NH_4^+$ and $K^+$ are not easily separated in an acidic buffer because they will have very similar electrophoretic mobilities. Additives such as 18-crown-6 can be added to the buffer to complex with and decrease the mobility of $K^+$, to improve the separation of $NH_4^+$ and $K^+$ [61,62].

Capillary and microchip electrophoretic methods have recently been used in field monitoring studies. The systems used in these methods include both microchip and capillary-based devices and use both manual and automated injection systems. Most field capillary electrophoresis systems were not designed specifically for $NH_4^+$ analyses, so we will not describe them in detail here. Field-deployable and portable electrophoresis instruments have been reviewed previously [63,64].

## 3. Non-chromatographic separation methods

Non-chromatographic separation methods for determining $NH_4^+$ can be divided into two categories. One contains methods involving extracting $NH_4^+$ derivatives that can be determined using an optical detection method. The other contains methods involving volatilizing $NH_3$ and then removing the $NH_3$ from the sample matrix. Non-chromatographic methods combined with flow-analysis techniques can be automated and used in the field or *in situ* [8,65]. Devices using passive sampling or paper-fluid techniques have been developed to allow low-cost field analyses to be performed.

### 3.1. Liquid-liquid and liquid-solid extraction

The main aim of using extraction techniques when analyzing $NH_4^+$ is to improve the sensitivity of the detection method. $NH_4^+$ concentrations in seawater, particularly open ocean water, are low (nanomoles per liter). Traditional indophenol blue (IPB) methods are not sensitive enough to determine $NH_4^+$ at such concentrations, so samples have been subjected to liquid-liquid extraction [66], liquid-phase microextraction [67], solid-phase extraction (SPE) [68–70], and cloud-point extraction [71]. IPB or ion-paired IPB compounds were extracted using organic solvents and the extracts analyzed spectrophotometrically in early methods [66]. However, liquid-liquid extraction using solvent is harmful to the environment and difficult to automate. Liquid-liquid extractions have therefore been replaced with liquid-phase microextraction [67] and SPE [68], which use less solvent and are more readily automated. Some sample pretreatment techniques (e.g., solvent bar microextraction) can also be used. Badiee et al. [72] described a revolving solvent bar microextraction device consisting of four hollow fibers containing 1-octanol (the acceptor phase) to extract IPB and cationic surfactant ion pairs. The method gave a preconcentration factor of 372 and a LOD of $4.5 \, \mu g \, L^{-1}$ ($0.26 \, \mu mol \, L^{-1}$).

Zhu et al. [73] described a flow-batch system for determining $NH_4^+$ in seawater on a ship and found LODs as low as $0.7 \, nmol \, L^{-1}$. The method involved using a SPE column to enrich a fluorescent compound formed through an OPA-sulfite-$NH_4^+$ reaction, then online elution and fluorometric detection. Reagent blanks for the method were quantified and interferences caused by amines and amino acids that can be present in seawater were investigated in a later study [74]. The mean $NH_4^+$ concentration in the reagent blank was $6.7 \pm 1.5 \, nmol \, L^{-1}$, which was a maximum of 27 % of background $NH_4^+$ concentrations in seawater samples from oligotrophic parts of the ocean. The method was very specific and could be performed on a ship. A method involving SPE preconcentration was used to prepare $NH_4^+$-free seawater for use as a carrier for flow analysis or as a matrix for standards [75].

### 3.2. Membrane-based separation methods

Being volatile, $NH_3$ can be isolated from a sample matrix using a gas-diffusion device made by sandwiching a gas-permeable membrane between a donor phase and an acceptor phase. A hydrophobic porous membrane such as polytetrafluoroethylene (PTFE) is used to prevent water and ions from passing through and to provide a large active membrane area and a short diffusion path to ensure that effective mass transfer can occur between the donor and acceptor phases. Membrane-based devices are compatible with flow-through analysis systems [76,77]. Systems involving gas diffusion devices and flow analysis that have been used to determine $NH_4^+$ are summarized in Table 1.

The $NH_3$ in the acceptor phase after membrane separation has been conducted can be determined after being subjected to classic

**Table 1**
Summary of flow-through analysis system with membrane-based gas diffusion device for the determination of $NH_4^+/NH_3$.

| Flow-through techniques | Separation device or membrane | Detection method | LOD | Linear range | RSD | Sample throughput | Sample | Reference |
|---|---|---|---|---|---|---|---|---|
| Flow injection | Microporous PTFE membrane or microporous polypropylene film (celgard 2500) | Spectrophotometry (Nessler's reagent) | – | – | – | 70 h$^{-1}$ | – | van Der Linden [78] |
| Continuous flow | Microporous PTFE membrane | Fluorescence (OPA) | 0.018 µmol L$^{-1}$ | 0.2–200 µmol L$^{-1}$ | 4.4% (1 µmol L$^{-1}$) 2.1 % (10 µmol L$^{-1}$) 1.8 % (100 µmol L$^{-1}$) (n = 5) | 10 h$^{-1}$ | River samples | Aoki et al. [79] |
| Flow injection | PTFE tape with a thickness of 45 µm | Spectrophotometry (bromothymol blue) | 1 µmol L$^{-1}$ | 1 - 100 µmol L$^{-1}$ | 3% (10 µmol L$^{-1}$) | 100 h$^{-1}$ | Canal water | van Son et al. [80] |
| Flow injection | PTFE (0.076 mm thick with either a 0.2 or 0.45 µm pore size) non-laminated Gore-Tex® hydrophobic | Spectrophotometry (phenol red) | 0.05 µmol L$^{-1}$ | <100 µmol L$^{-1}$ | < 2% (2 µmol L$^{-1}$, n = 28) | 60 h$^{-1}$ (5 min for five successive measurements). | Seawater and crab excretion | Willason and Johnson [81] |
| Flow injection | Microporous hydrophobic PTFE membrane (0.45 µm pore size) | Fluorescence (OPA) | 1.5 nmol L$^{-1}$ | To at least 2 µmol L$^{-1}$ | < 1.8 % (n = 12) | < 30 h$^{-1}$ | Freshwater, salt water and interstitial waters | Jones [82] |
| Flow injection | PTFE gas-permeable membrane | Conductometry (HCl as receiving solution) | 0.1 µmol L$^{-1}$ | 0.1–100 µmol L$^{-1}$ | 3.9% (5 µmol L$^{-1}$) 1.7 % (10 µmol L$^{-1}$) 1.4 % (50 µmol L$^{-1}$) | 60 h$^{-1}$ | Fresh water And salt water | Hall and Aller [83] |
| Flow injection | Gas-diffusion cell (diffusion path = 240 mm × 1.5 mm). | Spectrophotometry (bromothymol blue, pH indicator) | 17 µg L$^{-1}$ NH$_3$-N | 0 - 5000 µg L$^{-1}$ NH$_3$-N | 0.7% - 2.1 % (n = 6) | – | River water | Clinch et al. [84] |
| Sequential injection | Celgard 2400 hydrophobic membrane | Spectrophotometric (Berthelot reaction and BTB pH indicators) | – | 0.05–350 mmol L$^{-1}$ | 5% - 7% (pH indicators) | – | Yeast fermentation medium | Lukkari et al. [85] |
| Flow injection | PTFE tape (width = 22 mm, thickness = 8−9 µm) | Spectrophotometry (bromothymol blue, pH indicator) | 0.6 mg L$^{-1}$, NH$_3$-N | 1 - 100 mg L$^{-1}$ NH$_3$-N | 3.4% (2 mg L$^{-1}$NH$_3$-N) 0.7% (80 mg L$^{-1}$ NH$_3$-N) (n = 10) | 28 min (6 injection) | Industrial liquid effluents. | Andrew et al. [86] |
| Flow injection | Four types of membranes: 1, ordinary PTFE plumbing tape; 2, PVDF Durapore® hydrophobic membrane (modified polyvinylidene fluoride, 0.22 µm pore size) 3, Fluoropore® (polytetrafluoroethylene with polyethylene backing,0.2 µm pore size) from Millipore; 4, Celgard 2500 (polypropylene, 0.04 µm pore size) from Celanese®. | Spectrophotometric (Berthelot reaction, Salicylate method and BTB pH indicators) and conductometric (deionized water and boric acid) | 0.03 – 1 mg L$^{-1}$ | < 60 mg L$^{-1}$ | 0.92% - 4% | – | Wastewater | Cerdà et al. [87] |
| Flow injection | PTFE tape (plumbers tape, 12 mm × 0.075 mm) | Fluorescence (OPA) | 7 nmol L$^{-1}$ | > 4 mmol L$^{-1}$ | 5.7% | 30 h$^{-1}$ | Estuary waters and seawaters | Watson et al. [88] |
| Flow injection | PTFE plumbing tape | Spectrophotometry (bromothymol blue, pH indicator) | 9 µg L$^{-1}$ (continuous-flow) / 3 µg L$^{-1}$ (stopped-flow mode) | 20 – 160 µg L$^{-1}$(continuous-flow) / 100 – 3000 µg L$^{-1}$ (stopped-flow mode) | 3% (continuous-flow) / 2%(stopped-flow mode) | 135 h$^{-1}$ (continuous-flow) / 60 h$^{-1}$(stopped-flow mode) | Estuarine waters | Gray et al. [89] |
| Multicommuted flow injection | PVDF Millipore Durapore® hydrophobic membrane (pore size of 0.45 µm) | Spectrophotometry (bromothymol blue, pH indicator) | 42 µg L$^{-1}$ | 50 - 1000 µg L$^{-1}$ | < 1.5 % | 20 h$^{-1}$ | Surface water and tap water | Oliveira et al. [90] |
| Multicommuted flow injection | PVDF Millipore Durapore® hydrophobic membrane (pore size of 0.45 µm) | Spectrophotometry (bromothymol blue, pH indicator) | 18 µg L$^{-1}$ | 50 - 1000 µg L$^{-1}$ | < 2.0 % | 20 h$^{-1}$ | Sea and estuarine samples | Oliveira et al. [91] |
| | Semi-permeable PTFE membrane (0.076 mm Thickness) | | – | – | – | – | – | Kolev et al. [92] |

| Technique | Membrane | Detection | LOD | Linear range | RSD | Throughput | Application | Reference |
|---|---|---|---|---|---|---|---|---|
| Sequential injection analysis | | Spectrophotometry (bromocresol green, pH indicator) | | | | | | |
| Pulsed flow by micro-solenoid pumps | PTFE pipe tape | Conductometry (HCl as receiving solution) | 0.2 μmol L$^{-1}$ (estuarine and coastal waters, in situ); 0.014 μmol L$^{-1}$ (shelf waters, in situ); | < 18 μmol L$^{-1}$ (coastal waters) < 2 μmol L$^{-1}$ (shelf waters) | 2.5 %–6 % | – | Estuarine, coast, shelf waters | Plant et al. [93] |
| Sequential injection | PVDF Durapore® membrane filter | Spectrophotometry (bromothymol blue, pH indicator) | 27 mg L$^{-1}$ | 0.1 – 5 mg L$^{-1}$ | < 2% | 23 h$^{-1}$ | Estuarine water and sea water | Segundo et al. [94] |
| Multisyringe injection | Hydrophilic PVDF membrane Durapore® (12 mm × 75 mm × 0.12 mm) | Conductometry (HCl or boric acid as receiving solution) | 45 μg L$^{-1}$ | 0.075–360 mg L$^{-1}$ | < 2% | 32 h$^{-1}$ | coastal seawater, Pond water, aqueous extracts of composts | Henríquez et al. [95] |
| Solenoid micropump system | The same as [95] | Conductometry (H$_2$SO$_4$ as receiving solution) | 0.27 μmol L$^{-1}$ | | < 1% | | Coastal water and drinking water | Henríquez et al. [96] |
| Flow injection | Four different types of membrane: 1, PTFE plumber's tape (thickness ≤ 0.2 μm); 2, PTFE bonded to polyethylene support (Fluoropore, Millipore, 0.2 μm); 3, PVDF (SureVent, Millipore, 0.1 μm); 4, PVDF (Durapore, Millipore, 0.22 μm) | Spectrophotometry (cresol red and thymol blue, pH indicators) | 8 μg kg$^{-1}$ | 0.1–5 mg kg$^{-1}$ | 6% (0.1 mg kg$^{-1}$) 2% (5 mg kg$^{-1}$) (n = 5) | 10 h$^{-1}$ | Solid building materials | Timofeeva et al. [97] |
| Programmable flow analysis system | SureVent® super hydrophobic gas-diffusion membrane (0.1 μm pore size) | Spectrophotometry (bromothymol blue, pH indicator) | 15, 88 and 440 nmol L$^{-1}$ (with sample volume of 2.0, 1.0, and 0.25 mL) | 0.028−5.6 μmol L$^{-1}$ (2.0 mL sample) 0.28−13.9 μmol L$^{-1}$ (1.0 mL sample) 1.4−55.6 μmol L$^{-1}$ (0.25 mL sample) | 0.71 %, 1.2 % and 0.97 % (2.0, 1.0 and 0.25 mL sample) (n = 10) | 20, 30, 40 h$^{-1}$ (2.0, 1.0, 0.25 mL sample) | Estuarine and coastal seawaters | Šraj et al. [98] |
| Flow injection | A commercial unit (Metrohm model 754) | Contactless conductivity detection (H$_2$SO$_4$ as receiving solution) | 1.85 μmol L$^{-1}$ | 2 - 30 μmol L$^{-1}$ | < 3.8 % (n = 20) | 20 h$^{-1}$ | Tap waters, river waters, and marine waters | Chaneam et al. [99] |
| Flow injection | PTFE gas-permeable membrane (47 mm i.d. with pore size 0.45 μm) | Spectrophotometry (orchid extract, pH indicator) | 2.12 mmol L$^{-1}$ (for high level NH$_4^+$) 0.76 mmol L$^{-1}$ (for low level NH$_4^+$) | 5 – 40 mmol L$^{-1}$ (for high level NH$_4^+$) 1 – 5 mmol L$^{-1}$ (for low level NH$_4^+$) | 0.48 % (20 mmol L$^{-1}$) 2.29 % (3 mmol L$^{-1}$) (n = 10) | 48 h$^{-1}$ (for high level NH$_4^+$) 15 h$^{-1}$ (for low level NH$_4^+$) | Wastewater and fertiliser | Sukaram et al. [100] |
| Flow through technique | PTFE Millipore membrane (Fluoropore, 0.22 μm, ø = 47 mm, thickness = 150 μm, porosity = 85 %, white, plain) | Conductometry (boric acid as receiving solution) | 10.2 μg L$^{-1}$ | 10.2 μg L$^{-1}$ - 500 mg L$^{-1}$ | < 1.71 % | ~54 h$^{-1}$ | Wastewater treatment process | Li et al. [101] |

IPB or OPA reactions. In 2014, Kodama et al. [102] described a membrane-separation continuous-flow system using a liquid waveguide capillary cell with a 1 m path length for determining $NH_4^+$ in seawater. The system had a LOD of $5.5 \pm 1.8$ nmol $L^{-1}$ and was linear up to 2000 nmol $L^{-1}$ when the detection wavelength was 630 nm and had a LOD of $13 \pm 5.3$ nmol $L^{-1}$ and was linear up to at least 10,000 nmol $L^{-1}$ when the detection wavelength was 530 nm. In 2018, Müller et al. [103] described an $NH_4^+$-selective fluoroionophore dye that could form a complex with $NH_4^+$ that fluoresced more strongly that the uncomplexed dye. The dye was mixed with an internal buffer and embedded in a hydrophilic polymer, then the polymer was covered with a PTFE membrane, as shown in Fig. 3. The dye had a connecting crown ether group, the cavity of which allowed only $NH_4^+$ to pass through. This method was satisfactorily selective for $NH_4^+$ and was insensitive to other amines.

Methods for analyzing $NH_4^+$ involving reactions with IPB or OPA are very selective and sensitive but are time-consuming and complicated. The pH or conductivity can be used to indicate the $NH_4^+$ concentration if a high degree of sensitivity is not required. For example, an $NH_3$ gas sensor with a glass pH electrode in the acceptor phase has been used widely [104,105]. However, sensors using pH electrodes are not suitable for field monitoring natrual waters due to a lack of sensitivity. Methods involving spectrophotometric measurements of pH indicators in the acceptor phase have been used in many applications (see Table 1). Chip-based diffusion systems have also been developed. The first chip-based gas-diffusion flow-injection analysis system was developed by Zhu et al. [106] using microfabricated electroosmotic pumps to transport the solutions. The system gave a LOD of 0.10 mg $L^{-1}$ (5.9 μmol $L^{-1}$) and a relative standard deviation <5 % at an $NH_3$ concentration of 4.0 mg $L^{-1}$. Šraj et al. [98] described an environmentally benign flow-through system for determining $NH_4^+$ in seawater. The system gave a LOD as low as 15 nmol $L^{-1}$. The reagents, including pH indicators, were inexpensive, non-toxic, and stored well.

The conductivities ($\sigma$) before and after $NH_3$ enters the acceptor phase can be used to indicate the $NH_3$ concentration. Strong or weak acids can be used in such a system. If a strong acid is used, the chemical reaction in the acceptor phase is

$$H^+ + NH_3 \rightarrow NH_4^+ \tag{1}$$

If excess acid is present in the acceptor phase, $\Delta\sigma$ is given by

$$\Delta\sigma = kC_{NH_4^+}(\lambda_{NH_4^+} - \lambda_{H^+}) \tag{2}$$

where $C_{NH_4^+}$ is the sorbed $NH_3$ concentration, $\lambda_{NH_4^+}$ and $\lambda_{H^+}$ are the equivalent ionic conductances of $NH_4^+$ and $H^+$, respectively, in solution, and $k$ is a constant dependent on the conductivity detector properties. In a dilute solution, $\lambda_{NH_4^+}$ and $\lambda_{H^+}$ will be close to the limiting equivalent ionic conductances ($\lambda_{NH_4^+}^\infty$ and $\lambda_{H^+}^\infty$, respectively). $\lambda_{NH_4^+}$ and $\lambda_{H^+}$ are markedly different ($\lambda_{NH_4^+}^\infty = 73.5$ S cm$^2$ equivalent$^{-1}$ and $\lambda_{H^+}^\infty = 349.82$ S cm$^2$ equivalent$^{-1}$) [105], and $\Delta\sigma$ will be negative because $\lambda_{NH_4^+} < \lambda_{H^+}$.

The high $\lambda_{H^+}^\infty$ value means a strong acid (which will give a high background conductivity) could give high baseline noise. The background conductivity is generally kept acceptable by using an acid concentration in the tens of micromoles per liter, which is close to the measured $NH_3$ concentration. The strong acid in the acceptor phase therefore needs renewing for each analytical cycle to prevent it becoming exhausted.

Using boric acid (to give low background conductivity) in the acceptor phase causes the reaction in the acceptor phase to be

$$H_3BO_3 + NH_3 \rightarrow B(OH)_4^- + NH_4^+ \tag{3}$$

and $\Delta\sigma$ to be

$$\Delta\sigma = kC_{NH_4^+}(\lambda_{NH_4^+} + \lambda_{B(OH)_4^-}) \tag{4}$$

meaning $\Delta\sigma$ is directly proportional to [$NH_4^+$] and will be positive.

A field analysis device with an acceptor solution not needing renewing was developed by Li et al. [107] using a solution with a high boric acid concentration (0.5 mol $L^{-1}$) to sorb $NH_3$. The system can determine the $NH_3$ concentration in real time using the conductivity profile derivative, then the $NH_3$ concentration, temperature, and pH can be used to determine the $NH_4^+$ concentration in the water sample (the donor) with a high degree of resolution. In 2018, Chaneam et al. [99] described a flow injection system for simultaneously determining the salinity, carbonate and $NH_4^+$ concentrations. A commercial gas diffusion unit with a circular PTFE membrane was used, and the acceptor solution was pure water. One advantage of the system was the use
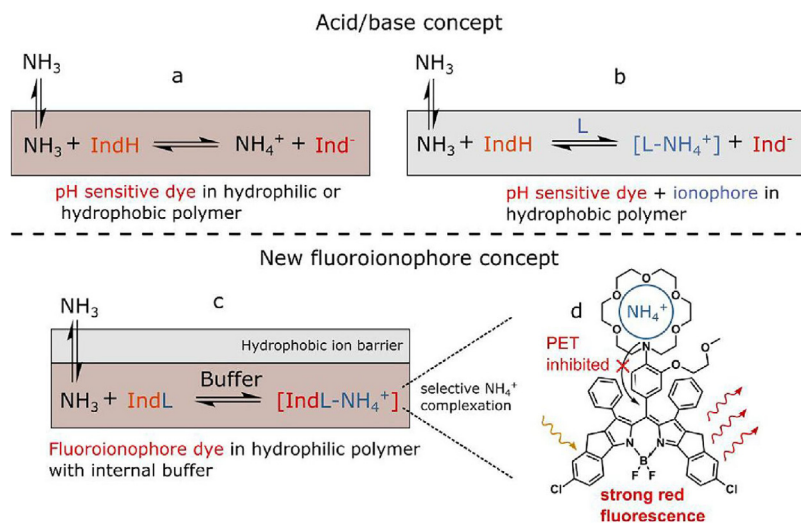


**Fig. 3.** Concepts of optical $NH_3$ sensing. a: Diffusion of $NH_3$ into a hydrophobic or hydrophilic matrix causes deprotonation of the immobilized pH indicator (IndH). b: Additional incorporation of a neutral ionophore (L) that is able to selectively complex and stabilize the formed $NH_4^+$ for higher selectivity and sensitivity. c: The new sensing concept based on an ion selective fluoroionophore embedded in a hydrophilic matrix and additional internal buffer. d: Chemical structure of the $NH_4^+$-selective fluoroionophore. Reproduced from [103] with permission of Elsevier.

of the contactless conductivity detection technique, meaning electrode contamination and fouling were avoided. The $NH_4^+$ LOD was 1.85 $\mu$mol L$^{-1}$, the throughput was 20 samples h$^{-1}$, and the relative standard deviation was <3.8 %.

### 3.3. Liquid-gas-liquid methods

The Kjeldahl method, in which $NH_3$ is distilled into a boric acid solution, is the classical liquid-gas-liquid separation method for analyzing $NH_3$. The Kjeldahl method is not as popular as membrane gas diffusion methods in systems used in research studies. Membrane-based gas diffusion gives effective mass transfer of $NH_3$ and allows automated flow-through detection to be achieved. However, the membrane may become clogged with particles or suffer biofouling, so regular maintenance is required. The membranes used are not compatible with organic solvents, surfactants, or high salinity samples, which cause leaks or short membrane lifetimes. Membraneless gas-diffusion units for flow analysis have therefore been developed [108–110].

Alahmad et al. [111] described a flow analysis system for determining $NH_4^+$ and sulfide. Vaporization and trapping were achieved using a membraneless vaporization unit with two cone-shaped reservoirs, one containing a donor phase and the other an acceptor phase. Two different units were used to separate $NH_4^+$ and sulfide. $NH_4^+$ entering the acceptor changed the solution conductivity, so could be detected using a contactless conductivity detection system.

In 2018, Giakisikli and Anthemidis [112] described a pressure-assisted dual-headspace microextraction technique. The entire liquid-gas-liquid extraction and fluorometry process were performed using a lab-in-syringe system with two syringe pumps and four selection valves. A sample was placed in one syringe and the acceptor solution in the other. The flexibility of the lab-in-syringe system allowed negative or positive headspace pressure to be generated using the pump to aspirate or dispense, respectively. This and heating and stirring the donor phase gave very efficient mass transfer between the phases. Micro-distillation of $NH_3$ and then dissolution of the $NH_3$ in a boric acid solution and analysis by conductometry has been performed [113]. Purge-and-trap pre-treatment then flow-injection fluorescence detection has been used to determine $NH_3$ in seawater [114]. This method was negligibly affected by primary amines and amino acids.

The acceptor solution is not always directly exposed to the gas phase. Valente et al. [115] introduced a method with a porous hydrophobic membrane between the acceptor and gas phases to avoid a sprayed sample entering the acceptor phase. A cylindrical PTFE module with a membrane at the bottom was used to contain a solution containing fluorometric reagents (OPA and $Na_2SO_3$). Headspace microextraction was performed using a standard 250 mL glass flask with a screw cap with a hole in. The cylindrical module was placed next to the hole in the cap to allow $NH_3$ to diffuse through the membrane into the acceptor solution.

A liquid drop method has been used to extract $NH_3$ from air samples or the headspaces of water samples since the 1990s by Dasgupta's group [116]. A change in the pH or conductivity of the drop is used to determine the $NH_4^+$/$NH_3$ concentration following the principle described in Section 3.2. In the first system that was developed [116], the exposed drop was withdrawn and analyzed in a flow-through absorption cell. The sample throughput was increased and carry-over effects decreased by performing on-drop detection in 1996 [117]. In 2015, Jaikang et al. [118] described an on-drop conductometry method for determining $NH_4^+$ in water samples. First, $NH_4^+$ in a sample was converted into $NH_3$ by adding a strong basic solution, then the sample was purged with nitrogen. A drop containing sulfuric acid in contact with a conductivity probe was used to extract $NH_3$ from the nitrogen. The rate at which the conductivity decreased was proportional to the $NH_4^+$ concentration in the sample. Šrámková et al. [119] described a single-drop headspace extraction and on-drop photometric sensing method. A modified laboratory-in-syringe system was used to automatically perform the microextraction and detection procedures. A photometric detector containing light emitting diodes and fiber optics was placed outside the syringe to allow on-drop sensing (Fig. 4). The method had a relative standard deviation of 6%, a linear range up to 25 mmol L$^{-1}$, and a LOD of 1.8 $\mu$mol L$^{-1}$.

Silver nanoclusters functionalized with citrate and glutathione are sensitive to changes in pH. A pH increase decreases the fluorescence intensity and absorbance [120]. A microextraction method has been developed in which a drop containing silver nanoclusters suspended on the cap of a centrifuge tube extracts $NH_3$ from the headspace of a sample and the $NH_4^+$ concentration in the original water sample is determined by analyzing the drop by fluorometry or UV/visible spectrometry [120]. The method was linear up to 350 $\mu$mol L$^{-1}$ and had a LOD of 336 nmol L$^{-1}$.

Microextraction of $NH_3$ has also been achieved using a liquid film with a high surface-area-to-volume ratio. In an early study [121], a liquid film containing sulfuric acid was used to extract $NH_3$ from breath, and the $NH_4^+$ concentration in the film was determined by conductometry. Fu and Zhang [122] introduced a method in which $NH_3$ was extracted using a black film 10−100 nm thick. The liquid film contained the pH-sensitive dye carboxy-seminaphthorhodafluor-1. $NH_3$ was quantified by measuring the
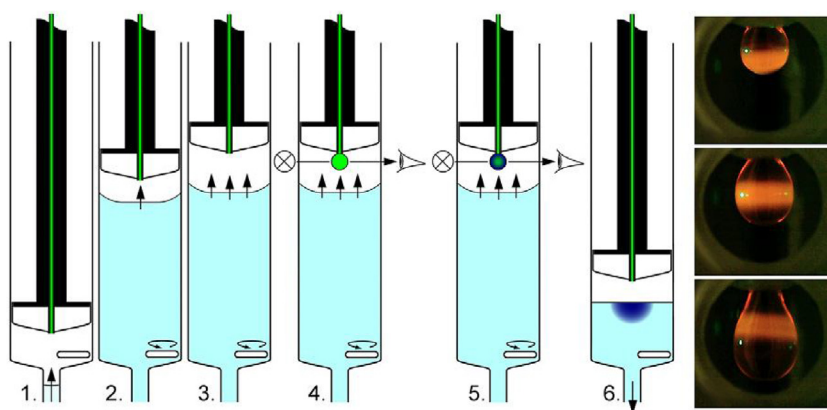


**Fig. 4.** Schematic representation of the syringe pump 1 and photographic images of a reagent drop during the individual analytical operations: (1) Aspiration of air and sample for head-space, (2) Aspiration of EDTA + NaOH, (3) Homogenization, starting evaporation of $NH_3$ and lowering the pressure to promote evaporation of $NH_3$, (4) Creation of a reagent drop, (5) Absorbance measurement, (6) Discharge of the syringe content and the reagent drop. Reproduced from [119] with permission of Elsevier.
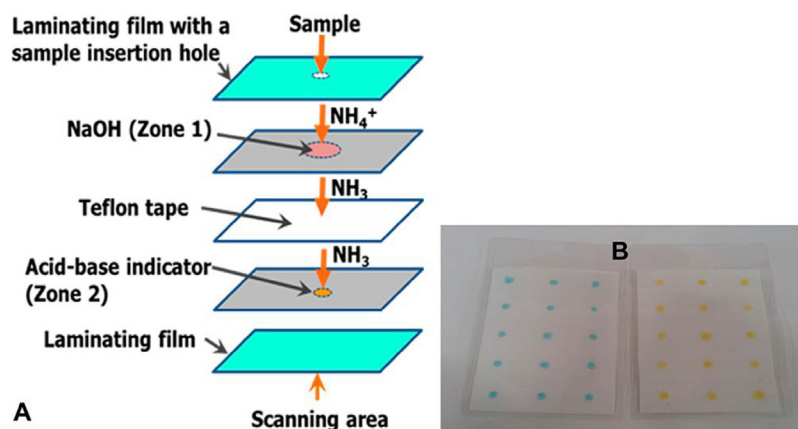
**Fig. 5.** (A) Schematic fabrication diagram of the proposed gas-diffusion μPAD (only a single set of sample and detection zones is shown). The diameters of zones 1 and 2 are 7 and 3 mm, respectively. (B) Photograph of the detection zone side of a bromothymol blue μPAD (left) and a 3-nitrophenol μPAD (right). Reprinted with permission from [127]. Copyright (2015) American Chemical Society (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

fluorescence of the dye, which was affected by the pH. Other volatile compounds (e.g., acetic acid and formaldehyde) could be determined using the same approach.

### 3.4. Other separation methods

Other separation methods, including gas-phase molecular adsorption spectrometry, paper-fluid and passive sampling, are summarized here. Isolated $NH_3$ can be directly measured by gas-phase molecular absorption spectrometry [123,124]. A method for converting $NH_4^+$ into $N_2$ and determining the $N_2$ concentration by atmospheric-pressure glow-discharge microplasma molecular emission spectrometry has been described [125].

Microfluidic paper-based analytical devices (μPADs) are cheap, easy to use, suitable for use in the field or remote areas, and environmentally benign [126]. μPADs can be analyzed by taking a digital photograph with a mobile phone or even by the naked eye. μPADs can therefore sometimes be used as completely instrument-free assays. μPADs have been used with various separation approaches to allow $NH_4^+$ to be analyzed.

In 2015, Jayawardane et al. used a gas-diffusion separation step in a μPAD fabricated by combining layers of several different materials (Fig. 5) [127]. The μPAD contained a Teflon membrane sandwiched between two filter papers. A sample and pH indicator were loaded onto each filter paper in a defined hydrophilic zone created by surrounding the zone with a hydrophobic agent. The paper and membrane were laminated between two films to maintain the patterned paper alignment and prevent the indicator solution evaporating. A change in indicator color was identified by scanning the μPAD using a desktop scanner. Two indicators, 3-nitrophenol and bromothymol blue, were used, and they had LODs expressed as the concentration of N of 0.8 and 1.8 mg L$^{-1}$, respectively (equivalent to 0.06 and 0.13 μmol L$^{-1}$, respectively).

In 2016, Phansi et al. [128] described a membraneless gas-separation μPAD in which, instead of a hydrophobic membrane, a 0.8 mm spacer layer (two-sided mounting tape) was sandwiched between the donor and acceptor layers. A small hole in the spacer layer allowed gas to diffuse through. The μPAD was used to determine $NH_4^+$ in wastewater and fertilizer. In 2019, Peters et al. [129] developed a more sensitive μPAD for analyzing freshwater. The device performed membraneless micro-distillation. The device consisted of two layers of paper with circular hydrophilic zones. The hydrophilic zone on one layer was impregnated with NaOH to act as a donor, and the hydrophilic zone on the other layer was impregnated with a pH indicator to act as an acceptor. The

μPAD with a μ-distillation chamber was twice as sensitive as a μPAD with a gas-permeable membrane.

Other methods involving filter papers impregnated with reagents used to extract $NH_3$ from a sample headspace have been described [130,131]. However, these were not strictly paper-fluid methods. The immobilized reagents included modified Berthelot's reagents [130] and butterfly pea flower extract (a pH indicator) [131].

Passive sampling techniques, which are used widely for environmental analyses, have also been used to analyze $NH_4^+$ and $NH_3$ [132,133]. A passive sampler separates and enriches the analytes of interest from a sample matrix during the deployment period to give a time-weighted average concentration. $NH_4^+$ or $NH_3$ can be passively sampled from environmental water in two main ways, using a cation-exchange membrane or film to remove $NH_4^+$ [134–137] and using a hydrophobic membrane to remove $NH_3$ [138].

Huang et al. [134] developed a passive sampler based on the diffusive gradient in a thin film technique to determine $NH_4^+$ in freshwater. The diffusion layer contained agarose and polyacrylamide hydrogels, which allowed $NH_4^+$ to pass through. The binding gel layer was agarose gel containing Microlite PrCH cation-exchange resin, which has a high $NH_4^+$ binding capacity. Passive samplers were deployed in the field, and the results obtained using the new samples and by analyzing spot samples agreed well. The method was improved by adding another resin (A520E resin for sorbing nitrate) to the binding layer and adding another binding layer (a Metsorb layer for sorbing phosphate) to allow $NH_4^+$, nitrate, and phosphate to be analyzed simultaneously by the passive sampler [135].

Almeida et al. [136,137] prepared a polymer inclusion membrane (PIM) using dinonylnaphthalene sulfonic acid as a carrier, poly(vinyl chloride) as a base polymer, and 1-tetradecanol as a modifier. PIM is a cation exchanger, and formed a semi-permeable barrier between the sample matrix and the receiving solution (HCl). $NH_4^+$ was extracted and transported through the PIM into the receiving solution. The PIM-based passive sampler was deployed in the field for 7 d, and the results strongly correlated with spot sampling results.

Ion-exchange-based passive samplers are not suitable for monitoring $NH_4^+$ in marine water. Alkali and alkaline earth metal cations are found at concentrations several orders of magnitude higher than $NH_4^+$ concentrations in marine water, so seriously interfere with ion-exchange of $NH_4^+$. A gas-diffusion-based passive sampler was therefore developed [138]. The sampler has porous

and hydrophobic membranes and can extract dissolved $NH_3$ from high ionic strength natural water.

## 4. Conclusions and perspectives

Analytical separation techniques have been used widely to determine $NH_3/NH_4^+$ in environmental water. Chromatographic methods can separate $NH_3/NH_4^+$ from amines, which can interfere with $NH_4^+$ determination using direct derivatization methods. However, chromatographic instruments are expensive and complex, and are therefore often unsuitable for field use. Non-chromatographic methods are more readily used in the field. Flow-through analysis methods are suitable for in situ or field use but cannot be deployed unattended for extended periods because they require electricity and because of the reagent and pump tubing lifetimes. Other instrument-free devices such as µPADs and passive samplers have been developed that are cheap, easy to use, environmentally benign, and suitable for use in remote areas.

Several challenges to determining $NH_4^+/NH_3$ need to be overcome. (1) Contamination. There is a strong risk of sample contamination and/or loss of analytes during sample collection, transfer, and storage. The $NH_4^+$ concentration may be affected by bioactivity in the sample, contamination by the atmosphere or the breath of the operator, or loss to the air when a frozen sample is thawed. (2) Sensitivity. In chromatographic methods, the sample injection volume is a balance between the sensitivity and separation efficiency. Mass transfer from the sample phase to the acceptor phase limits the sensitivity of a non-chromatographic method. (3) Matrix effects. Some separation methods, particularly chromatographic methods, are difficult to directly apply to very saline water. Coupling such methods to other separation process (e.g., gas diffusion or SPE) improves saline sample analysis.

Despite these challenges, there is great promise for the use of separation techniques when determining $NH_3/NH_4^+$. A method suitable for the requirements of the given monitoring task, the analyte concentrations, and the sample matrix should be selected.

### Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

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