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Ion pair-based liquid-phase microextraction combined with cuvetteless UV–vis micro-spectrophotometry as a miniaturized assay for monitoring ammonia in waters

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ABSTRACT

A miniaturized method based on liquid-phase microextraction (LPME) in combination with microvolume UV–vis spectrophotometry for monitoring ammonia in waters is proposed. The methodology is based on the extraction of the ion pair formed between the blue indophenol obtained according to the Berthelot reaction and a quaternary ammonium salt into a microvolume of organic solvent. Experimental parameters affecting the LPME performance such as type and concentration of the quaternary ammonium ion salt required to form the ion pair, type and volume of extractant solvent, effect of disperser solvent, ionic strength and extraction time, were optimized. A detection limit of 5.0 $\mu g\,L^{-1}$ ammonia and an enrichment factor of 30 can be attained after a microextraction time of 4 min. The repeatability, expressed as relative standard deviation, was 7.6% ($n = 7$). The proposed method can be successfully applied to the determination of trace amounts of ammonia in several environmental water samples.

1. Introduction

Ammonia is an important source of inorganic nitrogen that occurs naturally in waters. There exist two species in water samples, toxic unionized ammonia (NH_3), when pH is above 9.75 and the relatively non-toxic ionized ammonium ion (NH_4^+) when the pH is below 8.75 [1]. Ammonia is considered as an important indicator of organic pollution, since large concentrations of ammonia in environmental samples can be ascribed to external discharge into the environment from domestic sewage, industrial wastes and fertilizer run-off [2]. Ammonia is toxic to fish and other aquatic life and can promote eutrophication of lakes, dams and other waters. Given its occurrence at trace level in many environmental samples, determination of ammonia has attracted increasing attention in environmental protection and agriculture.

Recently, several analytical techniques have been reported for the determination of ammonia in natural waters including UV–vis spectrophotometry [3–6], spectrofluorimetry [7], diffuse reflectance spectroscopy [8,9], ion-chromatography with fluorimetric detection [10], capillary electrophoresis with conductivity detection [11] or photometric detection [12], and electrochemical methods [13,14]. The standard methods more commonly used for the determination of ammonia in waters are the spectrophotometric methods based on the Berthelot reaction [15–17]. In these methods, samples are treated with phenol and an oxidizing agent, typically alkaline hypochlorite, along with an appropriate catalyst, to yield an intensely blue indophenol dye, which is then determined spectrophotometrically. In the reaction, the addition of a catalyst such as nitroprusside [15], manganese sulfate [16] or acetone [17] is necessary to improve the sensitivity at short reaction times. Bearing in mind the relatively low sensitivity of spectrophotometric methods and the low levels of ammonia in water samples, a preconcentration method is commonly needed prior to its determination. Several sample preparation methods such as PTFE-type membrane filter [3], mixed micelle-mediated extraction (mixed-MME) [4], micro-phase sorbent extraction and membrane filter (MF, a type of SPE) [5], solid-phase extraction (SPE) [8,9], headspace single-drop microextraction (HS-SDME) [12], have been used for extraction and preconcentration of ammonia. Nevertheless, the majority of these methods are time consuming and require elaborate sample preparation procedures.

Liquid-phase microextraction (LPME) approaches, firstly introduced by Liu and Dasgupta in 1995 [18], have rapidly gained in importance in analytical chemistry as a result of the important advantages that they provide for sample preparation. In LPME, a microvolume of extractant phase is used to extract and precon-

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centrate the analytes, besides allowing sample clean-up. Other advantages of these miniaturized methods include simplicity of operation, low cost and enhanced greenness profile as compared to conventional methods.

The combination of LPME with UV–vis spectrophotometry constitutes a considerable advance to improve conventional colorimetric methods that show low sensitivity and/or large solvent consumption when liquid-liquid extraction is involved. Because the extractant phase volume (~10 μL or less) does not fit with the volume needed to perform a measurement in conventional UV–vis spectrophotometers (~1 mL), the direct coupling of these techniques could involve an important dilution, and therefore the partial loss of the achieved enrichment factor. To overcome these shortcomings, a miniaturized cuvetteless UV–vis spectrophotometer system, where a drop is hold in place by surface tension [19] can be employed to perform microvolume spectrophotometric measurements with no dilution as demonstrated in previous publications [20–28].

The aim of this work is to propose a new method for the determination of ammonia using LPME to carry out the separation and preconcentration of ammonia in combination with microvolume UV–vis spectrophotometry. The proposed methodology is based on the extraction of the ion pair formed between the blue indophenol, obtained according to the Berthelot reaction, and a quaternary ammonium salt into a microvolume of organic solvent followed by spectrophotometric measurement with a commercial confined drop-based system.

2. Experimental

2.1. Reagents

All chemicals were of analytical reagent grade. Deionized water obtained from a Milli-Q water purifier (Millipore, Molsheim, France) was used throughout. A stock standard solution of ammonium (1000 mg L^{-1}) was prepared from ammonium acetate (Merck, Darmstadt, Germany). Working standards were prepared by suitable dilution of the stock standard solution prior to use.

The phenol–acetone solution was prepared by dissolving 7 g of phenol (Merck) in 1.5 mL of ethanol (Prolabo, Paris, France), adding 2 mL of acetone (Prolabo), and making up to volume with ethanol. Solutions of 30% (w/v) sodium hydroxide and 2% (v/v) sodium hypochlorite were prepared by dissolving the appropriate amounts of the respective reagents (Prolabo) in water (sodium hydroxide solution was boiled for 10–15 min in an open vessel to remove traces of ammonia). The sodium phenolate solution was prepared by mixing 10 mL of phenol-acetone solution with 10 mL of 30% (w/v) sodium hydroxide solution, and making up to a volume of 50 mL.

Two different quaternary ammonium salts, namely, tetrabutylammonium bromide (TBAB) (Sigma Aldrich, Steinheim, Germany) and hexadecylytrimethylammonium bromide (CTAB) (Sigma–Aldrich, St. Louis, MO, USA) were used to form an ion pair.

Six organic solvents, i.e., chloroform (Panreac, Barcelona, Spain), dichloromethane (Panreac), carbon tetrachloride (Panreac), carbon disulfide (Probus, Madrid, Spain), bromobenzene (Aldrich, Steinheim, Germany) and tetrachloroethylene (Aldrich) were tested as potential extractant phases. Acetone (Prolabo), methanol (Prolabo), ethanol (Prolabo) and acetonitrile (Prolabo) were tried as disperser solvents.

2.2. Apparatus

A Nanodrop® (Thermo Scientific, Wilmington, USA) Model ND-1000 spectrophotometer (optical path length ~1 mm) was used to perform determinations in microvolumes. Absorption peak measurements were carried out at 650 nm.

A commercially available 10-μL syringe containing a guided-PTFE plunger (Hamilton model 1701 RN, 10 AL) was used to remove a portion of the extract and to place it onto the pedestal of the Nanodrop® spectrophotometer.

A SIGMA 2-16 Versatile Centrifuge (Montreal Biotechnologies Inc., Dorval, Canada) was used to speed up phase separation after microextraction.

An UVIKON XS UV/VIS spectrophotometer (Secoman, Domont, France) equipped with conventional sample cells (optical path length ~1 cm) was used for ammonia determination in accordance with the conventional method [17].

2.3. Water samples

Different natural water samples were analyzed in this work: mineral water, spring water, tap water, lake water, river water, dam water and well water. Tap water and lake water were collected at the University of Vigo, placed at about 10 km far from the Vigo Ria (NE Atlantic Coast). River water and dam water were collected in Zamáns (Vigo). Well water was obtained from a well located in Vilanova do Hio, inside the Aldán Ria (NE Atlantic Coast). Water samples were stored at 4 °C and analyzed within 24 h of collection after filtration.

2.4. Procedure for ammonia determination

A 25-mL sample was placed in a 50 mL Erlenmeyer flask, 1 mL of sodium phenolate solution and 0.4 mL of sodium hypochlorite solution being added with thorough mixing after each addition. The resulting solution is then diluted to the mark with water and covered with plastic wrap of paraffin wrapper film. The Berthelot reaction was carried out at room temperature within 30 min. A 5-mL aliquot of the indophenol blue solution was transferred into a 15 mL polyethylene conical tube and 1 mL of 0.1 mol L^{-1} TBAB solution was added. After injecting 50 μL of chloroform as extractant phase into the aqueous sample, the mixture was manually shaken for 1 min. Separation of the two phases was accelerated by centrifugation for 3 min at 3000 rpm. At the end of the LPME process, a sedimented phase volume of 10 ± 2 μL was obtained at the bottom of the conical centrifuge tube. The supernatant aqueous phase was easily decanted with a Pasteur pipette. Then, 2 μL of the sedimented phase were removed with a microsyringe and subsequently placed onto the pedestal of the Nanodrop® spectrophotometer. The sample absorbance at 650 nm was determined against a reagent blank.

3. Results and discussion

In the Berthelot assay, a condensation reaction takes place between ammonia and phenol, then yielding indophenol blue in the alkaline media and in the presence of an appropriate oxidizing agent. In this work, the determination of ammonia is based on the LPME of an ion pair formed between indophenol blue and a quaternary ammonium salt with subsequent UV–vis spectrophotometric detection. The influence of different experimental variables such as type and concentration of the quaternary ammonium salt, nature and volume of the extractant phase, type and volume of the disperser solvent, salt addition and microextraction time were fully optimized.

3.1. Optimization of LPME

3.1.1. Type and concentration of the quaternary ammonium salt

Two different quaternary ammonium salts, TBAB and CTAB were tried to form an ion pair with indophenol blue dye followed by

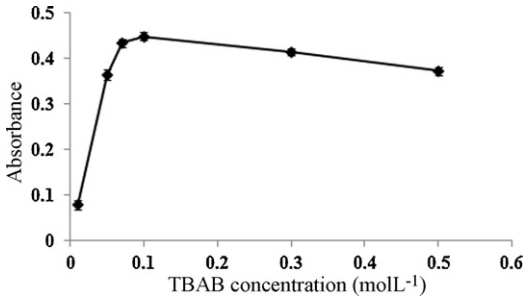

Fig. 1. Effect of the TBAB concentration.

their extraction in an organic solvent. Only TBAB did form an ion pair extractable by chloroform under the experimental conditions employed. Thus, TBAB was selected as ion-pair forming agent.

The concentration of TBAB was then studied in the range of 0.01–0.5 mol L^{-1}. Results shown in Fig. 1 revealed a strong increase in the extraction efficiency with increasing concentration of TBAB up to 0.1 mol L^{-1}. However, a further increase in the TBAB concentration gave rise to a slight decrease in absorbance that can be attributed to the increase of the sedimented phase volume. A 0.1 mol L^{-1} TBAB concentration was consequently used for further experiments.

3.1.2. Type of the extracting solvent

The requirements for the organic solvent in LPME are immiscibility and low solubility in water, as well as high extraction efficiency of target analytes. Organic solvents with larger density than water were selected for being easily removed from the bottom of the centrifuge tubes at the end of the LPME process. Thus, chloroform, dichloromethane, carbon tetrachloride, carbon disulfide, bromobenzene and tetrachloroethylene were tested as extractant phases in this work. Different volumes (between 40 and 100 μL) of each extractant solvent were used in order to achieve a final common volume of sedimented phase of 15 μL. Among the organic solvents tried, carbon tetrachloride, dichloromethane, carbon disulfide and tetrachloroethylene were not able to extract the ion pair, chloroform being the only organic solvent capable of extracting the ion pair under the experimental conditions used in this study. Consequently, chloroform was selected as the extracting solvent for further experiments.

3.1.3. Volume of extracting solvent

The volume of extractant phase has a great impact on the potential enrichment factor attainable in LPME. Therefore, the influence of the amount of chloroform used was investigated. Taking into account the relatively large solubility of chloroform in water (8.5 g L^{-1}), experiments were performed using initial volumes of chloroform ranging from 50 to 100 μL. As shown in Fig. 2,

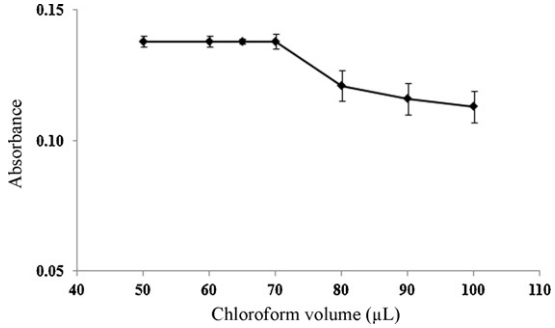

Fig. 2. Effect of the chloroform volume.

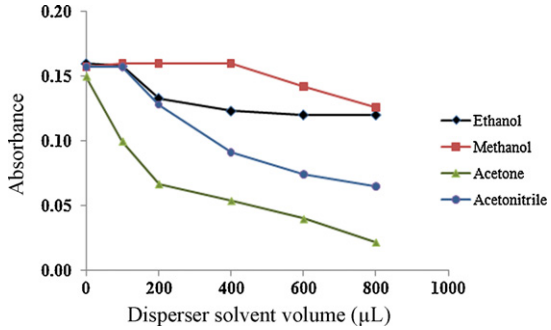

Fig. 3. Effect of the disperser solvent volume.

the signal obtained decreases on increasing volume of the extractant phase in the range of 65–100 μL as a result of the dilution of the extract. Volumes lesser than 50 μL were not selected because of the difficulty in removing minute quantities of sedimented phase with a microsyringe. In subsequent experiments, 50 μL of extractant phase was used.

3.1.4. Effect of the disperser solvent

Disperser solvents can play an important role in LPME procedures since they allow the formation of a cloudy solution that may enhance the extraction kinetics [29]. The use of a disperser solvent in combination with the extractant phase constitutes the basis of an LPME approach named as dispersive liquid-liquid microextraction (DLLME) [30]. The dispersive solvent must be miscible with both aqueous sample and extraction solvent. Thus, ethanol, methanol, acetone and acetonitrile were tested as disperser solvents using chloroform as extractant phase. Experiments were performed using different volumes of disperser solvents, ranging from 100 to 800 μL, keeping constant the sedimented phase volume (15 μL) for comparison purposes. As can be observed in Fig. 3, the use of a disperser solvent did not give rise to improvements in the analytical signal, on the contrary, a decrease in the extraction efficiency of the ion pair was noted. This negative effect can be attributed to the decrease in the partition coefficient of the ion pair into the extractant phase caused by the presence of disperser solvents [31]. Hence, the use of a disperser solvent was considered unsuitable in this work.

3.1.5. Salting-out effect

Addition of salt to the sample solution increases the ionic strength. Two main competitive effects occur in LPME when an increase in the ionic strength takes place, namely, salting-out effect and change of the physical properties of the Nernst diffusion film [32]. In the case of the salting-out effect, salt addition has a favourable impact on the extraction, since it decreases water solubility of the analyte, thus improving mass transfer to the organic phase. On the contrary, it has been reported that the diffusion rate of the analyte into the extractant phase may decrease due to the change in the properties of the Nernst diffusion film. Furthermore, it should be taken into account that the addition of salt reduces the water solubility of the extractant phase, thereby involving the dilution of the enriched extract at increasing concentrations of salt. Thus, for comparison purposes, the effect of salt addition was studied keeping a fixed volume of sedimented phase (15 μL). The concentration of NaCl added to the sample solution was studied in the range of 0–20% (w/v). As shown in Fig. 4, salt addition causes a negative effect on the extraction of the ion pair, which is more pronounced at large NaCl concentrations. Therefore, further experiments were performed without salt addition.

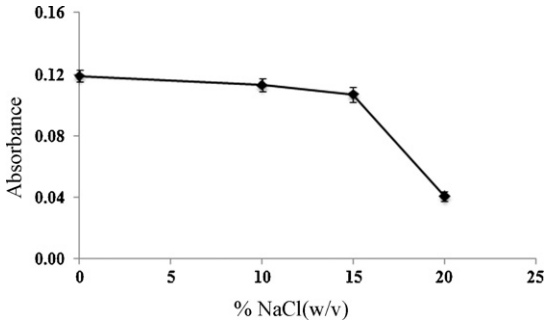

Fig. 4. Effect of the ionic strength of the sample.

3.1.6. Effect of extraction time

Extraction time is usually a key parameter in LPME due to its time-dependent nature. Results revealed that the microextraction time, defined as the interval between injection of the extractant solvent and the start of centrifugation, does not affect the extraction efficiency of LPME in the range studied (1–5 min). This indicates that the extraction process is very fast, probably due to the large surface of contact between the extraction solvent and the aqueous phase. In this method, the most time-consuming step is the centrifugation used for phase separation (3 min at 3000 rpm). In subsequent experiments, the phase separation by centrifugation was performed after 1 min of microextraction.

3.2. Analytical performance

Linearity of the calibration function, limits of detection and quantification, repeatability and enrichment factor of the proposed method were investigated under the optimal LPME conditions.

Ten calibration standards in the range of 20–700 $\mu g\,L^{-1}$ were run. The equation for the linear range of the calibration function was: $Y = 0.0013[NH_4^+] + 0.0156$, where Y is absorbance and $[NH_4^+]$ is the concentration of ammonia in $\mu g\,L^{-1}$. The regression coefficient (R) was 0.9991.

The detection (LOD) and quantification (LOQ) limits, calculated as $3\sigma/m$ and $10\sigma/m$ (σ being the standard deviation of 10 blank measurements and m, the slope of the calibration line), were 5.0 and 16.7 $\mu g\,L^{-1}$, respectively.

Precision of the proposed method, expressed as relative standard deviation (RSD), was evaluated in terms of repeatability and was found to be 7.6%. Precision of the Berthelot's reaction before DSDME was also evaluated, and found to be 0.7%.

The enrichment factor, defined as the ratio of the slope of the calibration line for the LPME method to that of the calibration line without preconcentration, was 30.

The extraction efficiency, defined as the percentage of the mass of analyte originally present in the sample which is transferred to the organic extractant phase at the end of the extraction process, was found to be about 6%.

Some characteristics of the proposed method, such as enrichment factor, LOD, precision and estimated analysis time were compared to those of different methods reported in the literature involving preconcentration and spectrophotometric detection of ammonia (Table 1). LPME provides adequate enrichment factor and working range, being the least time-consuming method. Precision is similar to that provided by other microextraction techniques reported in the literature. In addition, the LOD is comparable to that reported in most procedures involving preconcentration in spite of the 10-fold lesser optical path of microvolume spectrophotometry.

Table 2
Determination of ammonia in waters.

Sample	Ammonia added ($\mu g\,L^{-1}$)	Ammonia found ($\mu g\,L^{-1}$)	Recovery (%)
Mineral water	–	<LOQ	
	50	49.3 ± 5.8	99 ± 12
	100	90.6 ± 6.4	91 ± 6
Spring water	–	<LOQ	
	50	67.7 ± 7.9	110 ± 13
	100	121.6 ± 9.4	109 ± 8
Tap water	–	<LOQ	
	50	50.8 ± 2.9	102 ± 6
	100	92.6 ± 3.3	93 ± 6
Lake water	–	42.5 ± 5.0	
	50	100.3 ± 8.3	108 ± 9
	100	143.8 ± 8.4	101 ± 3
River water	–	85.4 ± 3.4	
	50	134.0 ± 13.2	99 ± 10
	100	173.8 ± 7.1	94 ± 4
Dam water	–	29.9 ± 1.1	
	50	87.9 ± 4.7	110 ± 6
	100	129.7 ± 16.3	101 ± 13
Well water	–	19.3 ± 0.8	
	50	65.7 ± 2.6	95 ± 4
	100	135.0 ± 10.7	113 ± 9

3.3. Analysis of water samples and recovery study

To demonstrate the applicability of our LPME approach, the method was tested for the determination of trace amounts of ammonia in mineral water, tap water, river water, lake water, well water, dam water and spring water samples. The analytical results are listed in Table 2. As can be seen, the ammonia concentrations in well water, river water, lake water and dam water samples were in the range of 19.3–85.4 $\mu g\,L^{-1}$, while the concentrations of ammonia in the remaining water samples were below the LOQ of the method.

A recovery study was performed in order to check for matrix effects. Water samples were spiked at two concentration levels, 50 and 100 $\mu g\,L^{-1}$. The recovery values are shown in Table 2. Satisfactory results were obtained in all cases, with recoveries ranging from 91 to 113%, hence indicating the absence of matrix effects. It should be highlighted here that addition of EDTA to the sample prior the Berthelot's reaction would be necessary to alleviate potential interferences such as Ca, Mg and Al [17].

Table 1
Comparison of the proposed method with other methods for determination of ammonia.

Enrichment procedure	Analytical technique	Enrichment factor	LOD ($\mu g\,L^{-1}$)	Linear range ($\mu g\,L^{-1}$)	Repeatability (RSD, %)	Estimated analysis time (min)	Ref.
PTFE-type membrane filter	UV–vis	4	2.5	10–160	3.0	–	[3]
Mixed-MME	UV–vis	28	1	2–125	2.8	20	[4]
MF (SPE)	UV–vis	5	1.2	5–150	1.0–6.5	40	[5]
SPE	UV–vis/DR	10	15	25–250	9.0	6	[7]
HS-SDME	CE-UV	14	27	90–1800	5.3–7.5	20	[12]
LPME	μvol-UV–vis	30	5	20–700	7.6	4	This work

4. Conclusions

In this work, a new method based on LPME coupled to microvolume UV–vis spectrophotometry has been developed for ammonia determination in natural waters. The LPME method is based on the formation of an ion pair and its further extraction in a microvolume of chloroform. Sample clean-up and preconcentration can be accomplished in a single step, showing appropriate sensitivity for trace level detection of ammonia in environmental samples. Other advantages of this method include ease of operation, low cost and enhanced greenness profile as compared to conventional methodology.

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