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Potentiometric analytical microsystem based on the integration of a gas-diffusion step for on-line ammonium determination in water recycling processes in manned space missions

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Graphical abstract

Highlights

- Life support system for human spaceflight missions.
- On-line chemical sensing in water recycling processes.
- Potentiometric determination of ammonium ion using a gas diffusion step.
- Samples of the Concordia station (Antarctica) grey water treatment plant

Abstract

The design, construction and evaluation of a versatile Cyclic Olefin Copolymer (COC)-based continuous flow potentiometric microanalyzer to monitor the presence of ammonium ion in recycling water processes for future manned space missions is presented. The microsystem integrates microfluidics, a gas-diffusion module and a detection system in a single substrate. The gas-diffusion module was integrated by a hydrophobic polyvinylidene fluoride (PVDF) membrane. The potentiometric detection system is based on an all-solid state ammonium selective electrode and a screen-printed Ag/AgCl reference electrode. The analytical features provided by the analytical microsystem after the optimization process were a linear range from 0.15 to 500 mg L^{-1} and a detection limit of 0.07 ± 0.01 mg L^{-1}. Nevertheless, the operational

features can be easily adapted to other applications through the modification of the hydrodynamic variables of the microfluidic platform.

Keywords: Lab on a chip, Polymer technology, Miniaturization, Gas-diffusion, Potentiometric detection, Ammonium ion.

1. Introduction

Water recycling systems are being developed by the European Space Agency (ESA), the Russian Federal Space Agency (ROSCOSMOS) and the National Aeronautics and Space Administration (NASA) to overcome the problem of water supply for long duration manned space missions [1-4]. The system proposed by ESA allows the conversion of urine, cabin condensate water and grey water (waste hygiene water) into hygiene water or even, if necessary, into drinking water by means of diverse processes such as nitrification, different filtration steps, reverse osmosis and remineralization. Ammonium ion is one of the compounds which must be taken into account because it is a product of urea decomposition and it is the precursor of the nitrification process, which is finally converted into nitrate ion by means of nitrifying bacteria. For this reason, a miniaturized analyzer for on-line monitoring is needed in order to verify the proper operation of the different stages of the water recycling process and to verify that the obtained water meets the requirements of the ESA water quality standards regarding ammonium concentration, both for hygiene and drinking water [2]. Figure 1 shows the scheme of the water recycling system for manned space missions proposed by ESA. The membrane filtration process is currently being tested in the Antarctic station Concordia to produce hygiene water from the grey water generated by the Concordia crew. The potential sampling points to monitor the ammonium ion are depicted.

Among the different published devices developed to detect ammonium ion, those that exploit the separation of ammonium as ammonia through a gas-diffusion membrane

have the greatest selectivity, providing a response practically free of interfering compounds [5-11].

Different hydrophobic membrane materials have been used such as polytetrafluoroethylene (PTFE) [5,7,8] and polyvinylidene fluoride (PVDF) [6,8-11], although the later has demonstrated higher mechanical resistance and analyte transfer rate [10].

Different materials have been used to fabricate miniaturized analyzers, such as glass, silicon, ceramics and polymers. However, only polymers allow an easy, economic and fast monolithic integration of gas-diffusion polymeric membranes in their fabrication process. One example is cyclic olefin copolymer (COC). This is because both glass and silicon substrates require high production costs and it is difficult to obtain three dimensional structures able to integrate hydrophobic membranes without leakage [12,13]. Whereas, low temperature co-fired ceramics (LTCC) are incompatible with the integration of polymeric membranes due to the high temperatures reached during sintering process [14]. In addition, polymer technology has other important advantages like an easy microfabrication of hermetically sealed three dimensional structures, chemical inertia against most acids and alkalis, the possibility to integrate conductive tracks and a good mechanical resistance [15-18]. In this way, these advantages allow the possibility to obtain robust and low cost microanalyzers of rapid prototyping and with low sample and reagents consumption by means of the monolithic integration of all components of the analytical process (pretreatment stages, microfluidics and detection system) on a single substrate [19]. Moreover, in order to achieve the higher level of autonomy and automation in the microanalyzers and minimize the involvement of the crew, the continuous flow techniques are the best option to implement. This provides a number of advantages such as simplicity, high speed of analysis, versatility and

robustness [6,19,20]. In addition, potentiometric detection systems such as ion-selective electrodes (ISEs) show good selectivity and enlarged working ranges. These overall features contribute to obtain repeatable and accurate responses [10,21,22].

There are some reported flow injection systems for the determination of ammonium ion using a gas-diffusion unit and potentiometric detection [5,10,22-24]. However, these experimental setups do not meet the miniaturization and automation requirements for manned spacecrafts, such as high integration level, high robustness, small size and low weight of the instrumentation and the possibility of an on-line monitoring without the need of human attention.

The goal of the present work is to develop a robust and selective potentiometric polymer based microanalyzer prototype to monitor the presence of ammonium ion, using the FIA technique. The device integrates microfluidics, a gas-diffusion module and a detection system in a single substrate and it is comparable in size to a credit card. The gas-diffusion module was integrated by a hydrophobic polyvinylidene fluoride (PVDF) membrane. The potentiometric detection system is based on an all-solid state ammonium selective electrode, and a screen-printed Ag/AgCl reference electrode. The prototype has been applied to analyze real effluents obtained from the grey water treatment plant located in the Antarctic station Concordia to verify its correct operation.

2. Experimental

2.1. Reagents and materials

The microanalyzer was fabricated with plaques and foils of COC from Topas Advanced Polymers (Florence, KY, USA) of different glass transition temperatures (T_g) and thicknesses: Topas 5013 plaques (1mm thickness, T_g 130 ºC) and Topas 8007 foils (25µm and 50µm thickness, T_g 75 ºC). A graphite-epoxy composite made of a mixture of graphite powder with a particle size of 50 µm (Merck, Germany), epoxy-resin

Araldite-M and a hardener HR (both from Ciba-Geigy, Spain) was used as a conductive support of ISE. For this purpose a graphite ink "Electrodag PF-407A" (Acheson) was also tested. The reference electrode was constructed by a screen-printed Ag/AgCl paste (Gwent, Pontypool, UK), testing also a conductive silver epoxy "CircuitWorks®" (Chemtronics) and a silver "EPO-TEK® H20E" epoxy (Epoxy Technology).

A hydrophobic gas-diffusion membrane made of PVDF with a 0.45μm pore diameter (Millipore, USA) was used to diffuse the analyte and separate it from the sample matrix.

Analytical grade reagents were employed for the evaluation of the microanalyzer. All solutions were prepared by weighing out and dissolving the corresponding salts in double distilled water.

Ammonium chloride (Panreac, Spain) standard solutions were prepared by successive dilutions of the 5,000 mg L^{-1} stock NH_4Cl. As reference solution, 0.1 M KCl (Sigma Aldrich, Germany) was used. 0.01 M tris(hydroxymethyl)aminomethane (Tris) (J.T. Baker, Holland) adjusted to pH 7.4 with hydrochloric acid (Sigma Aldrich, Barcelona, Spain) was used as a conditioning acceptor solution and 0.1 M NaOH (Fisher Chemical, UK) with 0.001 M ethylenediamine tetraacetic acid (EDTA) (Panreac, Spain) was used as basic complexating solution. This solution mixed with the sample/standard solutions is the donor solution.

Nonactin, bis(1-butylpentyl)adipate (BBPA), polyvinyl chloride (PVC) and tetrahydrofuran (THF), obtained from Fluka (Barcelona , Spain), were used for the preparation of the ammonium sensor membrane.

2.2.Fabrication of the microanalyzer

The fabrication process regarding COC-based devices used is described in detail elsewhere [25] and consists of four main steps: prototype design, pattern machining,

integration of different elements (such as electrodes and PVDF membrane) and final lamination. CAD software was employed for the prototype design (Figure 2A). It consisted on five layers (1xa, 1xc, 1xe, 1xg and 1xi) that, once overlapped, form the three-dimensional structure required for this application. The dimensions of the microanalyzer were 50.8 x 66.6 x 4.5 mm. The prototype (Figure 3) included four liquid inlets (a, b, c, d) and two outlets (w_2, w_3). Through the first two inlets (c, d), the carrier solution (d), where the sample is injected, and the NaOH solution (c) enter into the microsystem and converge in a T-shape confluence point. After that, they mix in a serpentine micromixer to obtain ammonia gas from ammonium ion present in the sample/standard solution. Then the mixed stream reaches the diffusion module, where a meander channel allows the ammonia gas to diffuse through the PVDF membrane to the acceptor channel, and finally, the solution at the bottom side reaches the waste outlet (w_2). The acceptor stream (b) on top (Tris adjusted to pH 7.4 with HCl) collects the ammonia gas and converts it to ammonium ion again. This solution reaches the detector and finally it is carried to the waste outlet (w_3). An auxiliary 0.1 M KCl solution is continuously pumped at 0.1 ml min^{-1} through the fourth inlet port (a) and flows through the channel in which the reference electrode is placed in order to keep its potential at a constant value [26]. This channel merges with the main channel after the detection chamber, acting thus as, a flowing liquid junction. The dimensions of the channels were 0.4 mm wide and 0.3 mm height and the diameter of the detection chamber was of 3.5 mm. The dimensions of the meander in the gas-diffusion module were 1 mm wide and 0.1 mm height, in order to maximize the contact area between the gas generated and PVDF diffusion membrane. The total microsystem and the detection chamber dead volumes were of 110 µL and 15 µL respectively.

Before machining the fluidic patterns, a first lamination of each TOPAS 5013 plaque of 1 mm with the corresponding TOPAS 8007 foil of 25 µm, which acts as an adhesive in the final lamination process, took place. The procedure can be described as follows: (see Figure 2A): foils b and d were laminated with plaque c, foil f was laminated with plaque g and foil h was laminated with plaque i. This was done in order that plaques and foils remained alternated in the final lamination process to achieve a perfect sealing. After that, all patterns (holes, channels and bas-relief for the working electrode) were machined onto the polymeric plaques by means of a CNC (computer numerically controlled) micromilling machine (Protomat C100/HF, LPKF, Spain).

The conductive epoxy resin used as a solid inner contact for the ISE was prepared by mixing Araldite-M and the hardener HR in a 1:0.4 weight ratio. After that, this mixture was also blended with graphite powder in a 1:1 weight ratio. The resulting conductive composite was placed in the corresponding bas-relief (5 in Figure 2C) and was cured at 40 °C for 24 h. Finally, the electrode was polished to obtain a smooth surface at the same level as the rest of the plaque, in order to be successfully laminated. The reference electrode was fabricated by screen-printing a Ag/AgCl paste, using a screen-printer machine (DEK 248, DEK, Spain), in a selected place over the auxiliary channel (d in Figure 2B). PVDF membrane was cut, washed with deionized water and ethanol, dried and placed correctly in its place (layer e in Figure 2A) with its more hydrophobic side facing down. As it can be seen in Figure 2B, some holes on the PVDF membrane are made so that during the lamination process, the 25 µm foil, which acts as adhesive, penetrates through the holes and seals microfluidics to prevent any leakage. COC layers alignment and final lamination were performed in a thermo-compression press (Francisco Camps, Granollers, Spain) at 102 ºC and 4 atm using aluminum support

plates with 4 alignment pins. Finally, fluidic connectors were fixed onto the polymer inlet/outlet ports with a holder and screws (Figure 2Ba).

The ammonium selective polymeric membrane was prepared by weighing out and mixing 1% nonactin, 65.5% BBPA, 33.5% PVC and 3 mL THF [27]. Membrane cocktail was deposited dropwise inside the corresponding cavity [Figure 2C4], which is defined over the epoxy-graphite composite and below the microchannels by following the next optimized protocol: 2 µL of membrane cocktail were added and let evaporated for five minutes. This was repeated until the cavity of the PVC membrane was filled. In this way, the formation of bubbles in the PVC membrane due to the THF evaporation is avoided. Finally, the detection chamber was sealed with an adhesive film.

2.3. Experimental setup

Figure 3 shows the continuous flow system setup. It consists of an external peristaltic pump (Minipuls 3, Gilson, Wisconsin, US) using Tygon® tubing (Ismatec, Wertheim, Germany) with 1.14 mm internal diameter and a six-way injection valve (Hamilton MVP, Reno, US). Teflon tubing (Scharlab, S. L., Cambridge, England) of 0.8 mm internal diameter was used to connect the external elements to the microsystem. Signal acquisition and data processing was performed by means of a customized potentiometer (6016 4-electrodes, TMI, Barcelona, Spain).

3. Results and discussion

3.1. Design and optimization of the microfluidic platform

3.1.1. Configuration of the gas-diffusion module

The main goal of this work is the development of a small sized, disposable, simple, selective and robust microanalyzer for ammonium ion, which monolithically integrates the microfluidic platform, the gas diffusion module and the potentiometric detection system, that meets all the requirements for the proposed application.

In order to achieve the best analytical features regarding sensitivity, baseline stability, noise and detection limit of the ISE and a long lifetime of the microsystem, different elements of the integrated diffusion module were optimized. The configuration of the detection chamber was optimized elsewhere [1].

Regarding the membrane module, PVDF membranes with different pore diameter (0.22, 0.45 and 1 µm) from Millipore were tested. As a compromise between the detection limit and lifetime, best results were obtained with 0.45 µm pore size. Another experimental finding observed was that the two sides of PVDF membrane had different wettability properties. Although the two sides were hydrophobic, one side was more hydrophobic than the other one, as it can be seen from the contact angle images obtained using water (Figure 4). This fact eventually causes that the membrane let pass the liquid from the less hydrophobic side to the more hydrophobic side, limiting the lifetime of the membrane and, therefore, limiting the lifetime of the whole microsystem. For this reason, it was decided to place the most hydrophobic side of the membrane down towards the channel of the donor solution containing NaOH with the sample so that, if the acceptor solution passes a little bit to the donor solution channel, a change in the signal response is not appreciated (it does not modify the composition of the solution that reaches the ISE), while if donor solution passes to the acceptor solution channel, the change of pH and ionic strength would modify the detector response.

Different shapes, depths and lengths of the diffusion module microchannels were evaluated. As described in previous works a linear [28] and meander [8,9] configuration can be used. In this sense, a linear microchannel with 100 µm depth, 1 mm width and 3 cm length and a meander microchannel with 100 or 200 µm depth, 1 mm width and 11 cm length were tested. Regarding to the variables to be optimized, better microsystem features were obtained with the meander configuration with 100 µm depth, 1 mm width

and 11 cm length. This can be explained due to the larger contact area between the membrane and the donor and acceptor solutions. The lesser depth of the microchannels also enhances the diffusion of generated ammonia and avoids its loss through the waste.

The inlet port position of the different solutions and their flow direction to the gas-diffusion module was also optimized. In this sense, first of all a commonly used configuration [6] consisting in the front entrance of both solutions was evaluated (Figure 5A) both in the same and counterflow liquid direction (Figure 5A). Results did not show a significant difference from reversing flow directions in terms of detection limits, baseline stability and noise. Thus, the counterflow direction was chosen, which simplified the microsystem design and fabrication. However, the effect the flow rate differences and the overpressure at the inlet ports, onto the PVDF membrane, reduce the membrane lifetime and therefore, the microsystem robustness is adversely affected. In order to protect the membrane integrity, a non-faced inlet port configuration (Figure 5B) was designed and tested. The experiments were performed only with counterflow configuration. In this case, liquid inlet ports are located at one side of the PVDF membrane and in the opposite side there is a COC wall, not a liquid output port, so that the membrane stress was reduced. The results showed that the overall microsystem features were unaltered, but the membrane lifetime was increased by more than 50 % even when flow rates of the different streams were quite different. For these reasons, this configuration was chosen as the optimal to proceed with the microsystem development.

3.1.2. Reference electrode and ISEs integration

In order to reduce and simplify the construction process of the ion selective and the reference electrodes, direct screen-printing of the conductive ink and pastes was used to avoid the use of more expensive and sophisticated technologies [29,30].

Two different materials were evaluated as conductive inner support for the fabrication of the all-solid state electrode: graphite ink Electrodag PF-407A and a graphite-epoxy composite. In the case of the reference electrode a Ag/AgCl ink C2030812D3, a conductive silver epoxy CircuitWorks® and a silver EPO-TEK® H20E epoxy were used. To characterize the features of these materials, standard adhesion tape tests [31] and lamination experiments were carried out and, in the case of the inks and pastes for the ISE, the PVC membrane deposition protocol and the feasibility of the membrane with the microsystem fabrication process were evaluated. In this sense, best results for the reference electrode were found with the Ag/AgCl ink C2030812D3 taking into account adhesion to the COC substrate and stability of the signal. As it expected [1], in the case of ISE, it was found that the conductive support which showed best results in terms of adhesion to both the polymeric substrate and the PVC membrane, was the graphite-epoxy composite. Consequently, better analytical features, such as sensitivity, repeatability and baseline signal stability, were achieved.

3.1.3. Evaluation of hydrodynamic and chemical variables

According to previous works [10,23], Tris adjusted to pH 7.4 was chosen as the acceptor solution. Chemical and hydrodynamic parameters were evaluated using a univariate optimization procedure in order to achieve a compromise between, working range, detection limit, reagent and sample consumption and sample throughput. Thus, the flow rate of the carrier, the basic and acceptor solutions was varied from 0.03 to 0.9 ml min^{-1} (when the flow rate of the 0.1 M KCl auxiliary solution was always kept at 0.1 ml min^{-1}) and the sample injection volume was varied from 25 to 580 µL. The concentration of NaOH in the basic solution was varied from 0.0001 to 1 M (keeping the concentration of EDTA fixed at $1 \cdot 10^{-3}$ M) and the concentration of TRIS in the acceptor solution was tested from 0.01 to 0.1 M. The optimal results were obtained using a flow rate of 0.4 ml min^{-1} for each channel (except to the one corresponding to reference electrode) and a sample injection volume of 225 µL. The composition of the

solutions was double distilled water, NaOH 0.1 M with EDTA 10^{-3} M and Tris 0.01 M for the carrier, the basic and the acceptor solutions, respectively.

Regarding the potential interfering compounds of the ammonium selective electrodes, methylated amines are the only ones that have to be taken into account because they are the only chemical interfering ions in a basic medium able to diffuse through the PVDF membrane [28]. However, these compounds are not present in the samples.

3.2. Analytical performance

Analytical features of the proposed microsystem were determined from calibrations obtained using different standard solutions of NH_4Cl. As example, Figure 6 shows the recorded signal for one of the calibrations performed. The obtained Nernst equation (using 3 calibrations data in consecutive days, with triplicates for each point; n = 15 and 95% confidence) was E = 320.3 (±1.3) + 59.4 (± 0.4) log [NH_4^+] with r^2=0.9993. Linear working range obtained was from 0.15 to, at least, 500 mg L^{-1}. The detection limit, according to IUPAC [32], was 0.07 ± 0.01mg L^{-1} (n = 9, 95% confidence). Repeatability studies were performed by successive injections of a 10 mg L^{-1} NH_4^+ standard solution (Figure 7). The relative standard deviation (n = 10, 95% confidence) of the signal was 0.3%.

Reproducibility was also tested from five calibrations experiments performed along one month. Mean slope of 58.90 with RSD value of 1.3% was achieved for the electrode, thus demonstrating the inter-day validation of the microsystem. These results showed the robustness and the reliability of the whole experimental setup. A sampling rate of 10 samples h^{-1} was obtained with the prefixed values of the hydrodynamic variables. Nevertheless, this factor should not be a limitation for the final application of the microanalyzer in manned space missions, where only a reduced number of samples per day should be analyzed. The microsystem lifetime was at least 6 months.

Slight modifications of the chemical and hydrodynamic variables of the proposed microsystem do not modify the main analytical features obtained, thus the robustness and the reliability of the whole experimental setup is shown. In this way, an easy adaptation of the proposed microsystem, in order to fit it to the different sample compositions or application constraints such as sample availability, reagent consumption, sampling rate, among others, can be carried out without losing its operational features.

3.3. Real samples analysis

Real effluents obtained from the grey water treatment plant placed in the Antarctic Concordia (AC) test station, where the conditions are very similar to those found in the space environment, were analyzed using the developed microsystem.

Specifically, the AC samples came from the output of the first reverse osmosis of the water recycling process [Figure 1] to demonstrate the suitability of the developed prototype microsystem to determine ammonium ion in this type of samples. Results obtained with the developed microsystem were validated by comparison with the ones obtained spectrophotometrically with the standard method based on indophenol blue [6]. Results obtained are shown in Table 1.

As it can be seen, in the case of AC samples, the obtained concentrations are not significantly different from the ones acquired with indophenol blue method by the use of a regression line (n=4, 95% confidence), obtaining as intercept a=0.2±0.2, as slope b=1.00±0.03, and as correlation coefficient of 0.9997. This confirms that the developed analytical microsystem is useful for the ammonium ion determination in recycled waters, even at lower concentrations than the allowed values by the legislation.

Conclusions

In this paper, a prototype of a microanalyzer for the determination of ammonium ion based on potentiometric measurements has been designed, developed, characterized and applied to real samples. The gas-diffusion module and the detection system have been optimized in order to achieve the required analytical features and to maximize operational autonomy and lifetime, which is needed at future manned space missions. In addition, the compatibility between COC substrate and different conductive inks such as epoxy-graphite composites (conductive supports of ISE) and Ag/AgCl paste (reference electrode) has been demonstrated. Moreover, configuration of the inlet streams in the gas-diffusion module allows a longer microsystem lifetime. In this way, the possibilities that the polymer technology offers for designing simply and robust miniaturized analyzers with integrated sample pretreatment stages has also been demonstrated for applications requiring a high miniaturization level.

The analytical features meet the requirements established in order to apply the microanalyzer for the on-line ammonium monitoring in future space applications [2].

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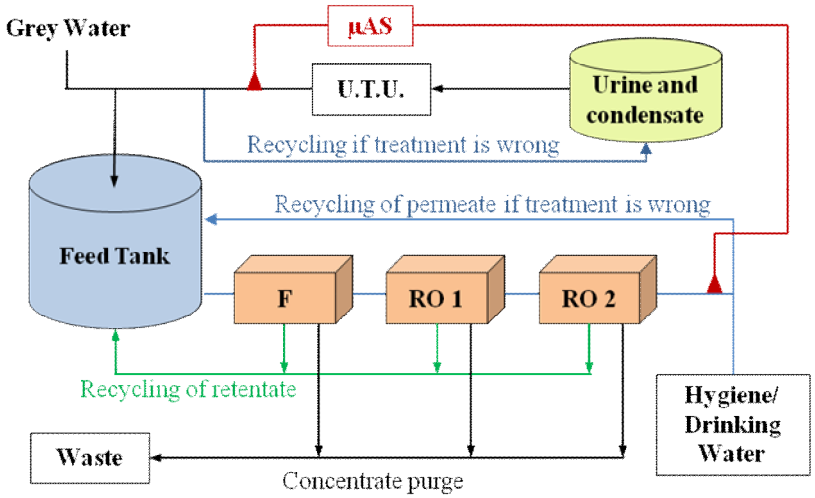

Figure 1. Scheme of the water recycling process. **U.T.U:** Urine treatment unit where the urea decomposition and the nitrification process take place; **F:** Filtration processes (ultrafiltration and nanofiltration); **RO 1:** First reverse osmosis; **RO 2:** Second reverse osmosis; **µAS:** Analytical microsystem developed in this work.

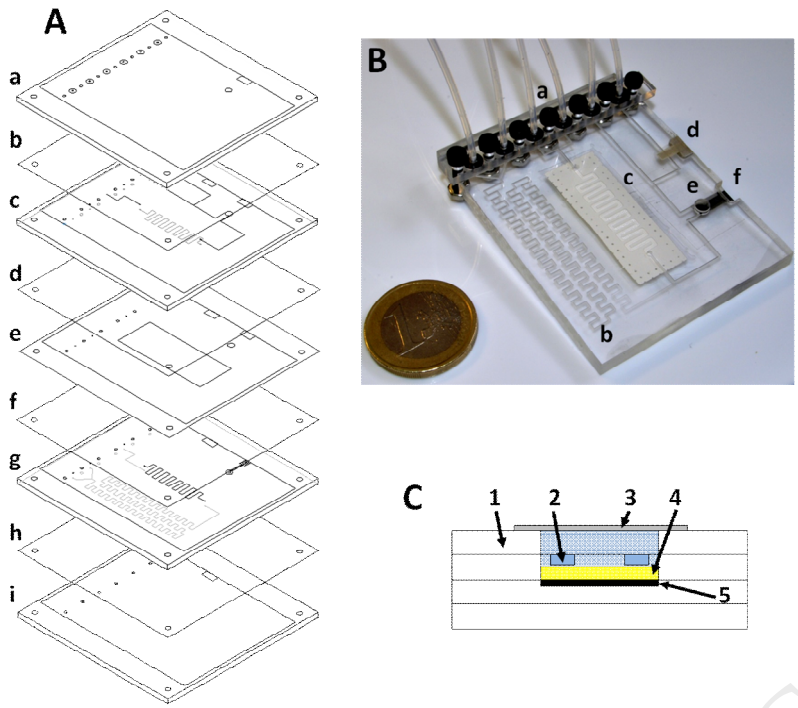

Figure 2. **A:** Layers design of the prototype. Layers a, c, g and i are Topas plaques of 1mm, layer e is Topas foil of 50 µm and layers b, d, f and h are Topas foils of 25 µm that acts as adhesive between plaques to encapsulate the microsystem. Layers c and g have patterns on both sides, in front, black color and behind, grey color; **B:** Picture of the final constructed device; **a)** Fluidic connections; **b)** Microfluidics; **c)** PVDF membrane; **d)** Reference electrode; **e)** Detection chamber; **f)** Working electrode; **C:** Front view of the detection chamber scheme; **1)** Polymeric layers; **2)** Microfluidic channel; **3)** Polymeric cover; **4)** Polymeric membrane; **5)** Epoxy-graphite composite as transducer.

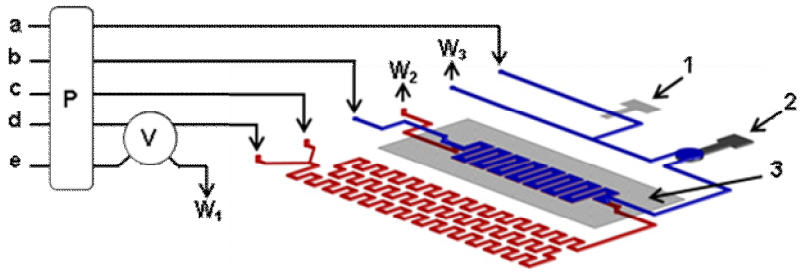

Figure 3. Schematic diagram of the microfluidic platform, the detection system and the experimental set-up. **a)** KCl 0.1 M auxiliary solution **b)** 0.01 M Tris acceptor solution at pH 7.4; **c)** 0.1 M NaOH solution with 10^{-3} M EDTA. **d)** H_2O as carrier solution; **e)** sample; **P)** peristaltic pump; **V)** six-way injection valve; **W)** waste outlets; **1)** reference electrode; **2)** working electrode; **3)** PVDF membrane; Red color: microchannels below the PVDF membrane; Blue color: microchannels over the PVDF membrane.

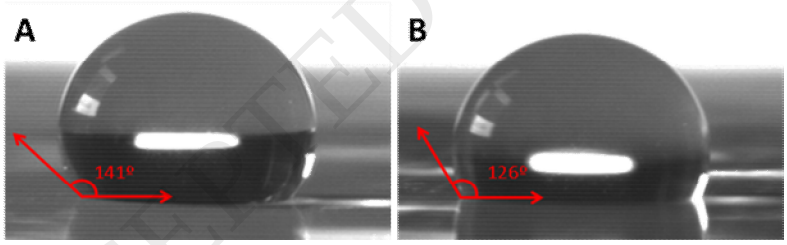

Figure 4. Photograph showing contact angles of water over the different sides of the PVDF membrane; **A**) The more hydrophobic side (141º); **B**) The less hydrophobic side (126º).

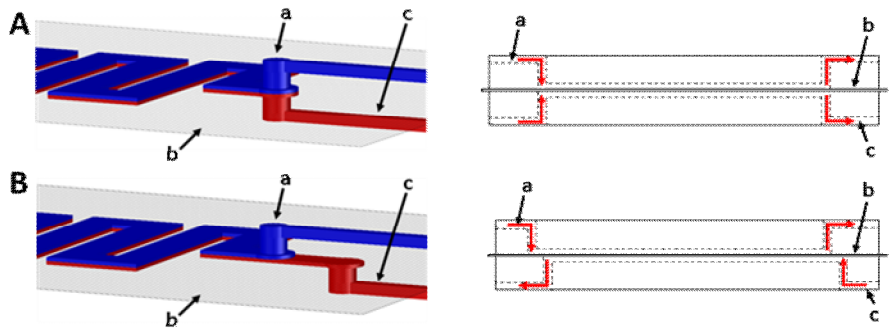

Figure 5. **A:** Three-dimensional and two-dimensional scheme of the integrated gas-diffusion module with faced liquid inlet ports; **B:** The same schemes with non-faced liquid inlet ports. In all images: **a)** Microfluidic channels over the membrane, where the diffused gas is collected and converted into ammonium ion; **b)** PVDF membrane; **c)** Microfluidic channels below the membrane, where the ammonia gas is generated; Red arrows show the flow direction.

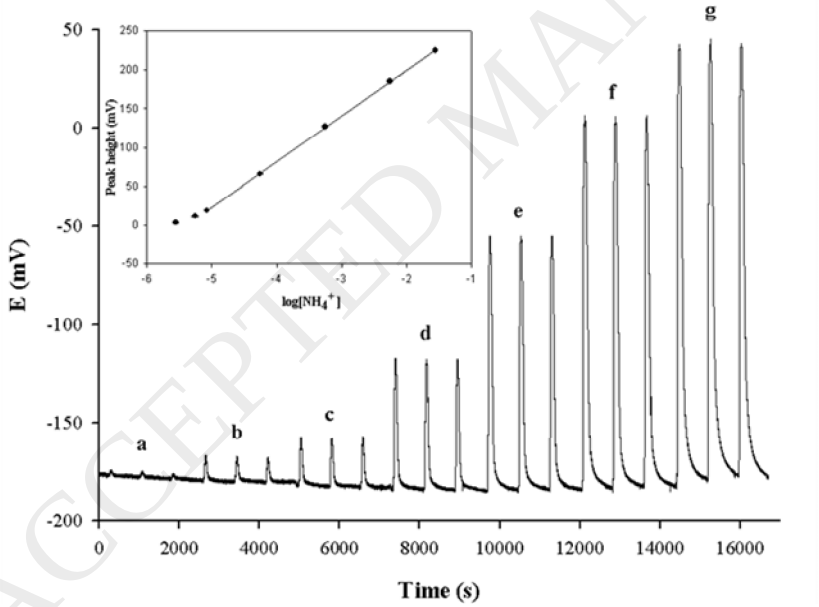

Figure 6. Signal recording and obtained calibration curve for the microanalyzer calibration using NH_4Cl standard solutions. NH_4^+ ion concentrations of 0.05 mg L^{-1} (**a**), 0.1 mg L^{-1} (**b**), 0.15 mg L^{-1} (**c**), 1 mg L^{-1} (**d**), 10 mg L^{-1} (**e**), 100 mg L^{-1} (**f**), 500 mg L^{-1} (**g**).

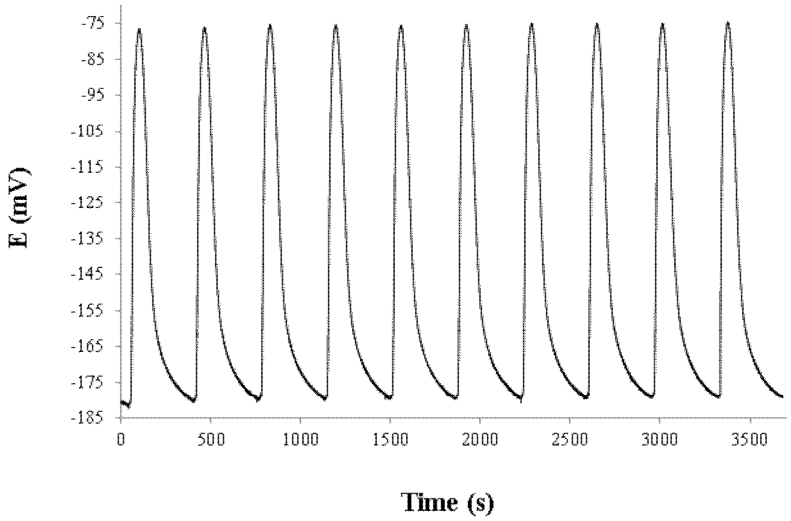

Figure 7. Signal recording for 10 injections of 10 mg L^{-1} NH_4^+ standard solution in order to calculate the microsystem repeatability.

Table 1 Concentration values in mg L^{-1} (n=3, 95%) from the analysis of real water samples from Antarctic Concordia test platform using the proposed microsystem.

Sample	**ISE**	**Indophenol blue**	**% error**
1	4.5 ± 0.2	4.3 ± 0.2	5
2	5.6 ± 0.4	5.4 ± 0.2	4
3	6.6 ± 0.3	6.4 ± 0.5	4
4	9.7 ± 0.3	9.5 ± 0.2	2

Table 1 Concentration values in mg L^{-1} (n=3, 95%) from the analysis of real water samples from Antarctic Concordia test platform using the proposed microsystem.