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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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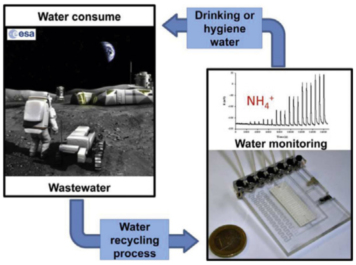
HIGHLIGHTS

- 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) gray water treatment plant.

GRAPHICAL ABSTRACT



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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 $\mathrm{mg\,L^{-1}}$ and a detection limit of $0.07 \pm 0.01\ \mathrm{mg\,L^{-1}}$. Nevertheless, the operational features can be easily adapted to other applications through the modification of the hydrodynamic variables of the microfluidic platform.

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 gray 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

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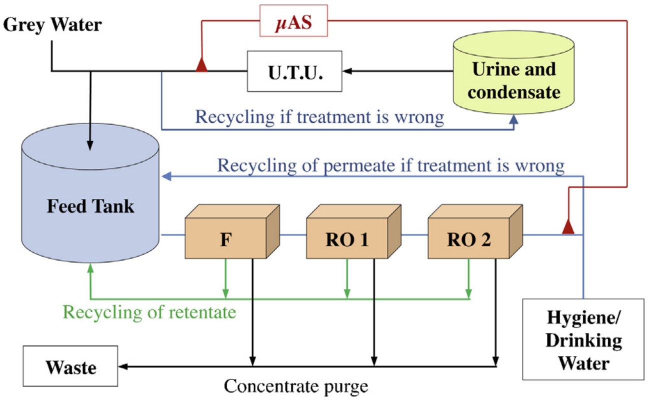

Fig. 1. Scheme of the water recycling process. U.T.U: urine treatment unit where the urea decomposition and the nitrification process take place; F: filtration processes (ultrafiltration and nanofiltration); RO 1: first reverse osmosis; RO 2: second reverse osmosis; μAS: analytical microsystem developed in this work.

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]. Fig. 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 gray 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], 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 gray 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 (1 mm thickness, T_g 130 °C) and Topas 8007 foils (25 μm and 50 μm thickness, T_g 75 °C). 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 0.45 μm 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 5000 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: