Analytica Chimica Acta 804 (2013) 190–196

Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: www.elsevier.com/locate/aca

Biparametric potentiometric analytical microsystem for nitrate and potassium monitoring in water recycling processes for manned space missions

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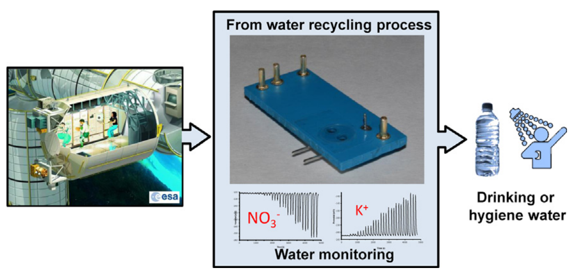
HIGHLIGHTS

- Life support system for human space-flight missions.
- On-line chemical sensing in water recycling processes.
- Microfluidic platforms for simultaneous potentiometric determination of nitrate and potassium ions based on the LTCC technology.
- Samples of the Antarctic Concordia station pretreatment plant.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 July 2013
Received in revised form
27 September 2013
Accepted 3 October 2013
Available online 16 October 2013

Keywords:
Lab on a chip
Low temperature co-fired ceramics technology
Miniaturization
Nitrate
Potassium
Potentiometric detection

ABSTRACT

The construction and evaluation of a Low Temperature Co-fired Ceramics (LTCC)-based continuous flow potentiometric microanalyzer prototype to simultaneously monitor the presence of two ions (potassium and nitrate) in samples from the water recycling process for future manned space missions is presented. The microsystem integrates microfluidics and the detection system in a single substrate and it is smaller than a credit card. The detection system is based on two ion-selective electrodes (ISEs), which are built using all-solid state nitrate and potassium polymeric membranes, and a screen-printed Ag/AgCl reference electrode. The obtained analytical features after the optimization of the microfluidic design and hydrodynamics are a linear range from 10 to 1000 mg L^{-1} and from 1.9 to 155 mg L^{-1} and a detection limit of 9.56 mg L^{-1} and 0.81 mg L^{-1} for nitrate and potassium ions respectively.

1. Introduction

One of the medium and long-term goals of space aeronautics is to conduct manned space flights of long duration [1]. This fact discards the possibility of transporting all the necessary metabolic consumables (including water, which is the first item in terms of mass) for the survival of the crew during the mission in the spacecrafts because this entails energy, space and mass limitations. To overcome this drawback, researchers and scientists try to find traces of water in the Moon or Mars with the intention that it could be used by future space explorers [2]. On the other hand, water recycling systems on board are being proposed by the European Space Agency (ESA), the National Aeronautics and Space Administration (NASA) and the Russian Federal Space Agency

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http://dx.doi.org/10.1016/j.aca.2013.10.013

(ROSCOSMOS) [3–5]. These systems generally allow the conversion of human liquid waste (urine), cabin condensate water and grey water (waste hygiene water) into hygiene water or even, if necessary, into drinking water. The ESA procedure consists in following diverse treatment procedures such as nitrification, ultrafiltration, reverse osmosis and remineralization.

To verify the proper operation of these water treatment units and that the resulting water meets the requirements of the ESA water quality standards [3] and does not accumulate certain chemical contaminants (e.g. metals and other minerals) water quality analyzers are needed. Taking into account the constraints associated to long term manned space missions, where mass is an issue, miniaturization of analytical systems [6,7] and the development of the so-called micro Total Analysis Systems (μTAS) is of great interest. They can be constructed with different materials such as glass/silicon, polymers and ceramics; the selection of which depends mainly on the final application and the development stage. For instance, tridimensional structures are difficult to obtain using glass and silicon substrates, glass present several limitations to integrate electronic circuits and fluidic channels and both technologies involve complex fabrication processes and clean room facilities [8,9]. On the other hand, polymeric materials show reduced thermal stability, low chemical stability in organic solvents, strong acids and bases and difficulties in the integration of electronic tracks [10,11]. Green tape ceramics or Low Temperature Co-fired Ceramics (LTCC) technology has demonstrated its usefulness as the substrate material for the miniaturization of analytical microsystems. It is possible to obtain complex structures with a multilayer approach, to easily integrate electronics, to achieve the hermetic sealing of microfluidic channels and have a good thermal and chemical stability [12–14]. In this way, the monolithic integration of all components of a microanalyzer (pretreatment stages, fluidics and electronics, detection system, among others) on a single substrate allows the possibility to obtain robust multiparametric analytical microsystems of rapid prototyping, low cost and with low sample and reagents consumption [15–21].

On the other hand, in order to minimize the involvement of the crew on the water quality measurements, microanalyzers must be as much autonomous and automated as possible. Thus, flow injection analysis techniques (FIA) provide a number of benefits in addition to those offered by the miniaturization of analytical processes with the LTCC technology, such as versatility, simplicity, the possibility to automate and connect the different stages of the analytical procedure and a high analysis throughput [22,23]. In addition, potentiometric detection systems such as ion-selective electrodes (ISEs) can be easily integrated in LTCC substrates, provide enlarged working ranges and, their enhanced selectivity allows the reduction of sample pretreatment stages, thus simplifying the microfluidic manifold [24,25].

The first step of the development of this work covers a limited list of analytes. Among some other analytical parameters, potassium and nitrate ions are considered as key indicators of the proper functioning of the water recycling system. Nitrate ion is a product of the nitrification process that converts the ammonium ion from urine into nitrate ion by means of bacteria and then is removed by diverse filtration steps such as ultrafiltration and reverse osmosis. Despite the fact that sodium and potassium can be both indicators of the proper functioning of the water purification and remineralization processes, potassium has been selected by ESA to monitor them. However, the list of parameters to be determined could be certainly modified/extended in the future to include sodium, if deemed necessary.

An on-line chemical water quality monitoring equipment to control the level of nitrate and potassium would give information of how efficient are the water purification and remineralization processes. Fig. 1 shows the scheme of the ESA water treatment process

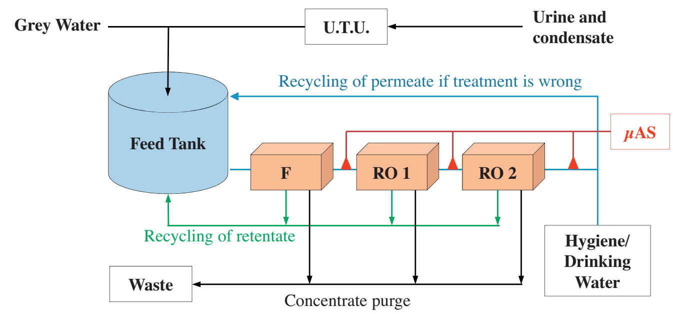

Fig. 1. Scheme of the water recycling process. U.T.U: urine treatment unit; F: filtration processes (ultrafiltration and nanofiltration); RO 1: first reverse osmosis; RO 2: second reverse osmosis; μAS: analytical microsystem developed in this work.

currently under development. The membrane filtration unit is currently being validated in the Antarctic Concordia station, where the conditions are very similar to those found in the space environment (i.e. isolation, scarcity of resources, closed environment, etc.). The location of the potential sampling points throughout the recycling process to be directed on-line to the biparametric prototype for nitrate and potassium ions is also depicted.

There are numerous reported works about the separate determination of nitrate and potassium ions using ISEs and FIA techniques in different matrices, such as food [26,27], fresh water [28], wastewater [29], fertilizers [29,30] and pharmaceuticals [29,31]. There are also two works that describe the simultaneous detection of both ions, one in mouthwash samples [32] and another in soil nutrient extract samples [33], using the potentiometric and FIA techniques. However, these experimental setups do not meet the requirements for manned spacecrafts: small size, low weight, high robustness and reliability of the instrumentation and the possibility of performing an on-line monitoring in unattended conditions.

The goal of the present work is to develop a robust LTCC-based potentiometric microanalyzer prototype to simultaneously monitor the presence of potassium and nitrate ion, using the flow injection analysis (FIA) technique. The device integrates microfluidics and the detection system in a single substrate and it is smaller than a credit card. The detection system is based on two ion-selective polymeric membrane electrodes, one for potassium ion and another one for nitrate, and a screen-printed Ag/AgCl reference electrode. The adequate performance of the prototype has been proved in effluents obtained from the water treatment plant placed in the Antarctic Concordia station.

2. Experimental

2.1. Reagents and materials

254 μm-thickness Dupont 951 green tapes were used as the substrate for the fabrication of the microanalyzer. Three different materials were evaluated as transducers and conductive tracks: Dupont 6146 (suitable for solderable tracks), Dupont 6145 (suitable for internal tracks) and a graphite-epoxy composite made of a mixture of graphite powder with a particle size of 50 μm (Merck), epoxy-resin Araldite-M and a hardener HR (both from Ciba-Geigy).

All reagents employed for the evaluation of the microanalyzer were of analytical grade. All solutions were prepared by weighing out and dissolving the corresponding salts in Milli-Q water. Potassium nitrate (Merck) standard solutions were prepared by successive dilutions of the 0.1 M stock KNO_3. 0.1 M KCl (Sigma–Aldrich) was used as the reference solution and 0.05 M Na_2SO_4 (Panreac) adjusted to pH 3 with sulfuric acid (Sigma–Aldrich) was used as conditioning solution.