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

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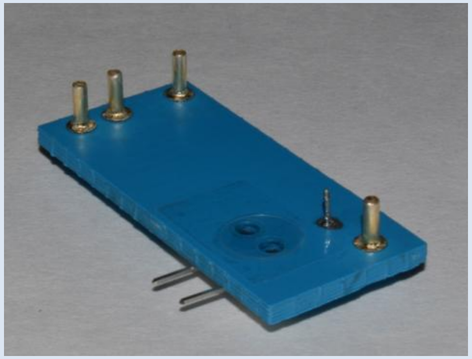
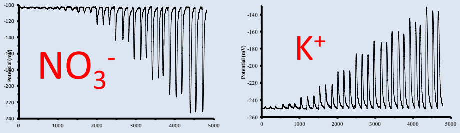
***Graphical Abstract**

From water recycling process





Water monitoring

Drinking or hygiene water

Life support system for human spaceflight 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.

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

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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 1,000 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.

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

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 (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. Figure 1 shows the scheme of the ESA water treatment process 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.

Tetraoctylammonium nitrate, Tris(2-ethylhexyl) phosphate (TEHP), polyvinyl chloride (PVC) and tetrahydrofuran (THF), obtained from Fluka, were used for the preparation of the nitrate sensor membrane.

Valinomycin, Bis(2-ethylhexyl) sebacate (DOS), Potassium tetrakis(4-chlorophenyl)borate, polyvinyl chloride (PVC) and tetrahydrofuran (THF), obtained from Fluka, were used for the preparation of the potassium sensor membrane.

2.2. Fabrication of the microanalyzer

The fabrication process regarding LTCC-based devices is described in detail elsewhere [15]. CAD software is employed for the prototype design (Figure 2A), where two separate identical devices are simultaneously fabricated. They consisted on thirteen layers (1xa, 1xb, 2xc, 1xd, 2xe and 6xf) that, once overlapped, provided the inner/outer three-dimensional structure required for this application. The final dimensions of each microanalyzer are 24.1 x 54.2 x 2.7 mm after firing. The prototype included three liquid inlets (Figure 3). Two of them converge in a T-shape confluence point. Sample is directly injected on a water carrier, which mixes with a highly concentrated buffered solution to keep the ionic strength constant. The mixed flow is carried to the detection chambers and finally to the waste outlet. An auxiliary 0.1 M KCl solution is continuously pumped at 0.2 ml min^{-1} through the third inlet in order to keep the potential of the reference electrode at a constant value [14], thus acting as a flowing liquid junction. The dimensions of the channels are 0.9 mm wide and 0.4 mm height, the diameter of the detection chambers is of 3 mm and the total microsystem dead volume is of 150 µL, all them after firing. The prototype was designed to minimize the distance of all electrodes and taking into account the required design of the microfluidic platform.

All patterns (holes and channels) were machined onto the green tapes by means of a laser ablation machine (Protolaser, LPKF, Germany). The reference electrode was fabricated by screen-printing a silver ceramic paste in a selected place over the auxiliary channel, using a screen-printer machine (DEK 248, DEK, Spain). Ceramic layers alignment and lamination was performed in a thermo-compression press (Francisco Camps, Granollers, Spain). Then, the devices were sintered in a programmable box furnace (Carbolite, Afora, Spain) and all elements that are not compatible with the sintering process were finally integrated as follows (Figure 2B): fluidic connectors were glued onto the LTCC inlet/outlet ports with epoxy glue and electrical connectors were soldered in their corresponding vias. The conductive epoxy resin used as a solid inner contact for the ISEs was prepared by mixing Araldite-M and the hardener HR in a 1:0.4 weight ratio. Later, the whole was also mixed with graphite powder in a 1:1 weight ratio. The resulting composite was placed in the corresponding cavity (Figure 2D) and was cured at 40 °C for 24 h.

The nitrate selective polymeric membrane was prepared following the previously optimized composition [34] by weighing out and mixing 6% tetraoctylammonium nitrate, 65% TEHP, 29% PVC and 3 mL THF. Likewise, the potassium selective polymeric membrane [30] was prepared by weighing out and mixing 1% valinomycin, 65.5% DOS, 0.5% Potassium tetrakis(4-chlorophenyl)borate, 33% PVC and 3 mL THF. Both membrane cocktails were deposited dropwise inside their corresponding cavity [Figure 2C and D], which is defined over the epoxy-graphite composite and by using the following optimized protocol: 2 µL of membrane cocktail were added and let evaporated while applying vacuum for five minutes. This was repeated until the cavities of the membranes were filled. Thereby, the formation of bubbles due to the THF evaporation is avoided. Finally, the detection chambers were sealed with a glass cover fixed with an adhesive film.

2.3. Experimental setup

The flow system setup is shown in Figure 3. It consists of an external peristaltic pump (Minipuls 3, Gilson, Wisconsin, US) equipped with 1.14 mm internal diameter Tygon® tubing (Ismatec, Wertheim, Germany) and a six-port injection valve (Hamilton MVP, Reno, US). 0.8 mm internal diameter Teflon tubing (Scharlab, S. L., Cambridge, England) was used to connect the external elements to the microsystem. For the acquisition and digital processing of the signal, a potentiometer and its software (TMI, Barcelona, Spain) were used.

3. Results and discussion

3.1. Design and optimization of the analytical microsystem

The main goal of the present work was the development of a simple and robust microanalyzer for nitrate and potassium ions, which monolithically integrates two potentiometric detection systems in the same microfluidic platform and that shares all the required solutions to carry out the chemical analysis in order to economize and reduce volumes of all liquids, taking into account the requirements for a manned spacecraft application.

To optimize analytical characteristics such as sensitivity and detection limit of the ISEs, two different detection chamber configurations were evaluated, one with a linear inflow profile (Figure 4A) and another one with a circular inflow profile (Figure 4E). As it can be demonstrated by the use of a fluorescent dye, the sample covers a larger surface of the ISE (Figure 4G) in case of using a circular inflow than in case of a linear profile (Figure 4C). With the first configuration, as well the peak heights and peak repeatability were increased as the peak broadening was better avoided (Figure 4D and 4H). Moreover, the circular flow profile removes more easily any formed bubble. Therefore, this configuration was chosen for further optimization of the microsystem.

The distance between the two working electrode membranes and the reference electrode is not a critical issue as far as the ionic strength of all the solutions in contact with the electrodes is high and the distance short. In the system, a good ionic conductivity along the microchannels, which connect both electrodes, was achieved by the use of concentrated salts (Figure 3).

Different materials were evaluated as the conductive inner support for the fabrication of the all-solid state electrodes. In the case of the reference electrode, a co-sintering ceramic paste of silver (DuPont 6146) was used [24]. In the case of the ISEs, two co-sintering ceramic silver pastes (DuPont 6146 and 6145) and a graphite-epoxy composite were tested. To characterize the response of the corresponding devices, calibration experiments were carried out by injecting 150 µl of KNO_3 standard solutions of increasing concentration. It was found that the best results in terms of peak heights, sensitivity, repeatability and baseline signal stability were obtained with the graphite-epoxy composite in both ISEs. This can be related to the better adhesion of the PVC ion-selective membrane with the graphite-epoxy composite since THF from the cocktail membrane can partially dissolve the epoxy surface during its deposition. In continuous flow conditions and using the co-sintering ceramic pastes, membranes slowly lift and lose their response characteristics with time due to poor electrical contact until they take completely off.

The influence of hydrodynamics and chemical variables has also been evaluated. According to previous works [31, 32], sodium sulfate was chosen as the conditioning solution because it provides better response features in terms of peak height and sensitivity to both ISEs. This fact is related to the lower value of the sodium and sulfate selectivity constants than the value of other ions commonly employed to adjust ionic strength for the employed ionophores.
Chemical and hydrodynamic parameters were evaluated using a univariate optimization procedure in order to achieve a compromise between the sensitivity of the analytical measurements, a proper linear working range for both ISEs and an adequate sample throughput.

Thus, the flow rate of the carrier and the conditioning solutions was varied from 0.4 to 1.2 ml min^{-1} (when the flow rate of the 0.1 M KCl auxiliary solution was always kept at 0.2 ml min^{-1}), the sample injection volume was varied from 50 to 500 µL and the conditioning solution was tested at concentrations ranging from 0.005 to 0.1 M. The optimal results were obtained using a flow rate of 0.8 ml min^{-1} for both the carrier and the conditioning solutions, a sample injection volume of 225 µL and a conditioning solution of Na_2SO_4 0.05 M . However, these parameters can be modified according to any different required sampling protocol.

Potentiometric selectivity coefficients ($logK_{i,j}^{pot}$) of potassium and nitrate were calculated using the fixed interference method with a 0.01 M concentration background of the interfering compounds except for NH_4^+, which was fixed to 0.001 M [35]. The obtained results (Table 1) showed the well-known interfering effect of HCO_3^- and Cl^- on the nitrate selective electrode and, NH_4^+ was the most interfering ion of the potassium selective electrode, which is based on a quaternary ammonium ionophore. This should not be as controversial because the maximum concentration of NH_4^+ in treated water is expected to be 0.5 mg L^{-1}, and therefore, its interference could be negligible at the expected level of potassium in potable and hygiene water (12 and 120 mg·L^{-1} respectively) [3]. However, HCO_3^- must be removed. Hence, the conditioning solution must be acidified to pH 3 with sulfuric acid to shift the acid-base equilibrium to carbonic acid [36]. Finally, Cl^- is a real interfering compound and its presence in the treated water represents a challenge for the accurate nitrate determination. According to the selectivity constant, if the ratio $[Cl^-]/[NO_3^-]$ is lower than 20, the interfering effect may be negligible. In the proposed application low chloride concentrations (lower than 10 mg L^{-1}) are expected, thus allowing the determination of nitrate, at the required concentrations with an adequate accuracy. In the case of a higher ratio, other solutions such as the integration of a chloride selective electrode in the microanalyzer, which allows a mathematical correction by means of the Nikolski-Eisenmann equation [24], could be implemented.

3.2. Analytical performance

Analytical features of the proposed microsystem were determined from successive calibrations. As example, Figure 5 shows the obtained recorded signal for one calibration. The obtained Nernst equations (n = 6 and 95% confidence) for each ion were E = -231.0 (±1.4) - 60.6 (± 0.5) log [NO_3^-] with r^2=0.996 and, E = 256 (±2) + 56 (± 1) log [K^+] with r^2=0.992. This linear working range corresponds to 10-1,000 mg L^{-1} and 1.9-155 mg L^{-1} for the nitrate and the potassium selective electrodes respectively (higher nitrate ion concentrations were not tested). The detection limits, which were calculated according to IUPAC by the intersection of the extrapolated lines of the Nernstian (high concentration) and nonresponsive (low concentration) segments of the calibration curve [37], were 9.56 ± 0.02 mg L^{-1} (n = 6, 95% confidence) for nitrate and 0.98 ± 0.07 mg L^{-1} (n = 6, 95% confidence) for potassium ion. Repeatability studies were performed by successive injections of two different KNO_3 standard solutions. The relative standard deviations of the signals were 1.8% (at 0.2 mM) and 1.5% (at 0.6 mM) for the potassium selective electrode and were 4.7% (at 0.2 mM) and 1.4% (at 0.6 mM) for the nitrate selective electrode. These results showed the robustness of the whole experimental setup, even when concentrations around the detection limit were used. Reproducibility was also tested from three calibrations experiments during the fifteen first days. Mean slopes of 59.5 and 55.5 with RSD values of 3% and 1.5% were achieved for nitrate and potassium electrodes respectively, thus demonstrating the inter-day validation of the microsystem.

Given the device configuration and the hydrodynamic parameters used, it was possible to obtain a sampling throughput of 30 samples h^{-1}, although this factor may not be a limitation for the final application of the microanalyzer in manned space missions. In fact, the reduction of reagents consumption and the microsystem maintenance are two of the most important goals to achieve. Further optimization will be performed in order to reduce reagents consumption by means of reducing flow rates, the frequency of the recalibration protocols and the sampling rate.

3.3. Real samples analysis

The microsystem was applied for the simultaneous determination of nitrate and potassium ions in effluents provided by ESA from the water recycling unit placed in the Antarctic Concordia station.

The analyzed water samples were obtained from the output of the first reverse osmosis stage (Figure 1). Results were validated by comparison with the ones obtained with inductively coupled plasma optical emission spectrometry (ICP-OES) [38] for potassium ion and ionic chromatography (IC) [39] for nitrate. Results obtained are shown in Table 2. In addition, chloride was measured by IC in order to verify its potential interference on the nitrate determination. A mean concentration of 18.70 mg L^{-1} was obtained.

In the case of nitrate, the concentration of three of the samples is under the detection limit. Tabulated values are estimated by fitting the experimental data to the non linear Nikolskii-Eisenmann equation and are less reliable than the obtained by the Nernst equation but approximate to the obtained ones acquired by the reference method. The resulting non-linear calibration equation (n = 6 and 95% confidence) is $E = -254.6\ (\pm 4.2) - 73.8\ (\pm 1.8) \log \left[[NO_3^-] + 3.1 \cdot 10^{-4}\ (\pm 3 \cdot 10^{-5})\right]$ with $r^2=0.994$. As it can be seen, at these low concentration values, which are under the ESA water quality requirements[1] for hygienic and drinking water (50 and 25 mg L^- respectively), the obtained concentrations are slightly higher than the ones acquired with ionic chromatography. This is related to the effect of chloride ion on the nitrate electrode response at nitrate concentrations near the detection limit. While in the case of potassium determination, the obtained results are not significantly different from the ones acquired with inductively coupled plasma optical emission spectrometry by the paired t-test (t_{calc} = 1.000; t_{tab} = 3.182; $t_{calc} < t_{tab}$). This confirms that the proposed analytical microsystem is useful for the simultaneous determination of nitrate and potassium ions in these samples.

Conclusions

In this paper, the possibilities that the LTCC technology offers to designing simply and robust miniaturized biparametric analyzers for applications requiring integration and small sizes has been demonstrated. A prototype of a microanalyzer for the simultaneous determination of nitrate and potassium ion based on potentiometric measurements has been developed, characterized and applied to real samples. The microfluidic platform and the detection system have been optimized in order to maximize operational autonomy, which is needed at manned space missions, and to achieve an adequate performance. Moreover, the compatibility between LTCC technology and epoxy-graphite composites used as conductive supports of ISEs has been also demonstrated.

The analytical features are in accordance with the requirements established in order to apply the microanalyzer for the on-line nitrate and potassium ions monitoring, with the aim of verifying the correct operation of the water recycling process (nitrification, ultrafiltration, nanofiltration and reverse osmosis) and determine the possible later use of the water as hygienic or even as drinking water after mineralization. In this sense, the research group is working on instrumentation compaction, changing conventional pumps and valves for miniaturized pumps and multicommutation microvalves. Furthermore, the triparametric system, which integrates the chloride ISE, is being developed for nitrate concentration correction.

Acknowledgments

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Table 1

Calculated potentiometric selectivity coefficients, $\log K_{i,j}^{pot}$, for K^+ and NO_3^- selective electrodes in treated water samples using the fixed interference method.

Main interfering compound (j) for K^+ selective electrode	$\log K_{i,j}^{pot}$
Na^+	-4.00
NH_4^+	-1.07
Ca^{2+}	-5.02
Mg^{2+}	-5.00

Main interfering compound (j) for NO_3^- selective electrode	$\log K_{i,j}^{pot}$
HCO_3^-	-1.93
Cl^-	-1.54

Table 2

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

Sample	Nitrate			Potassium		
	LTCC ISE	IC	% error	LTCC ISE	ICP-OES	% error
1	3.0 ± 0.4	1.82	61.1	3.2 ± 0.2	3.32	3.3
2	4.1 ± 0.4	2.88	40.6	3.9 ± 0.4	3.99	2.8
3	8.8 ± 0.5	7.82	12.6	6.9 ± 0.3	6.94	0.4
4	14.2 ± 0.6	13.31	6.7	9.9 ± 0.4	10.2	2.5

Figure 1

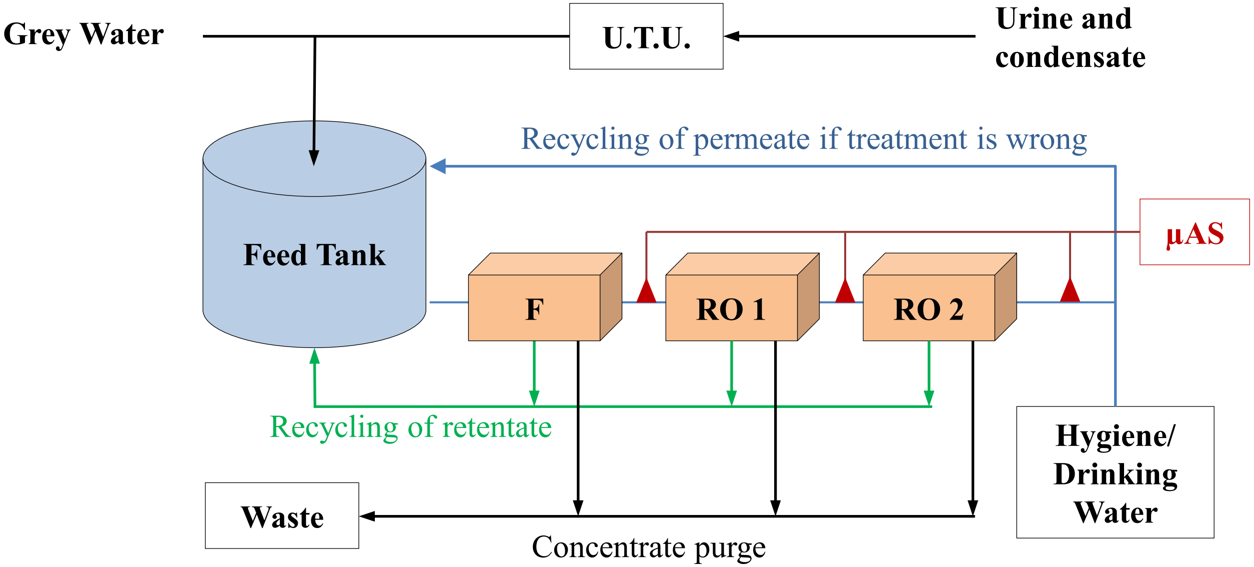
Grey Water
U.T.U.
Urine and condensate
Recycling of permeate if treatment is wrong
Feed Tank
µAS
F
RO 1
RO 2
Recycling of retentate
Hygiene/ Drinking Water
Waste
Concentrate purge

Figure 2

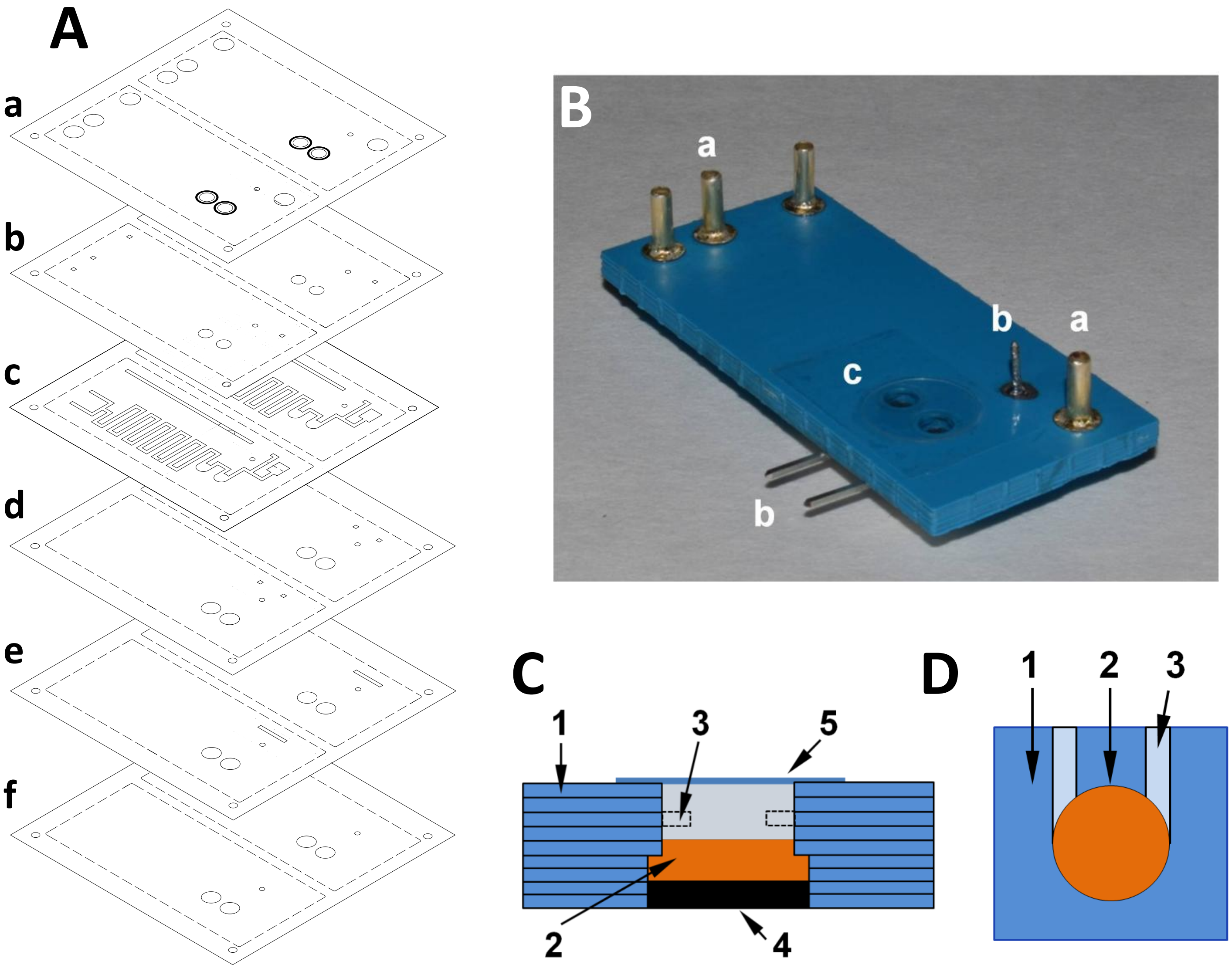

Figure 3

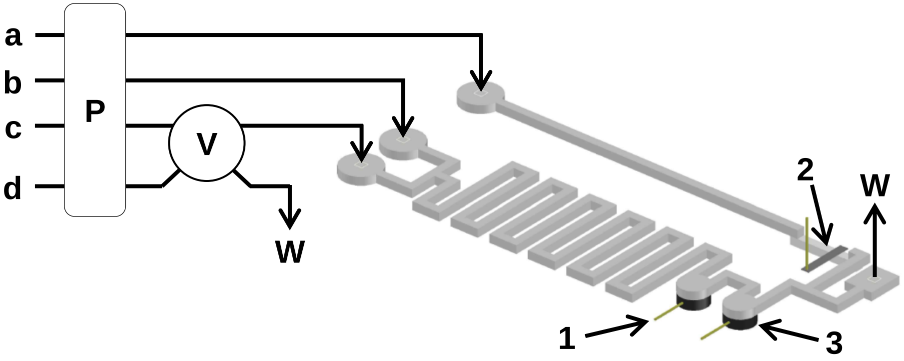

Figure 4

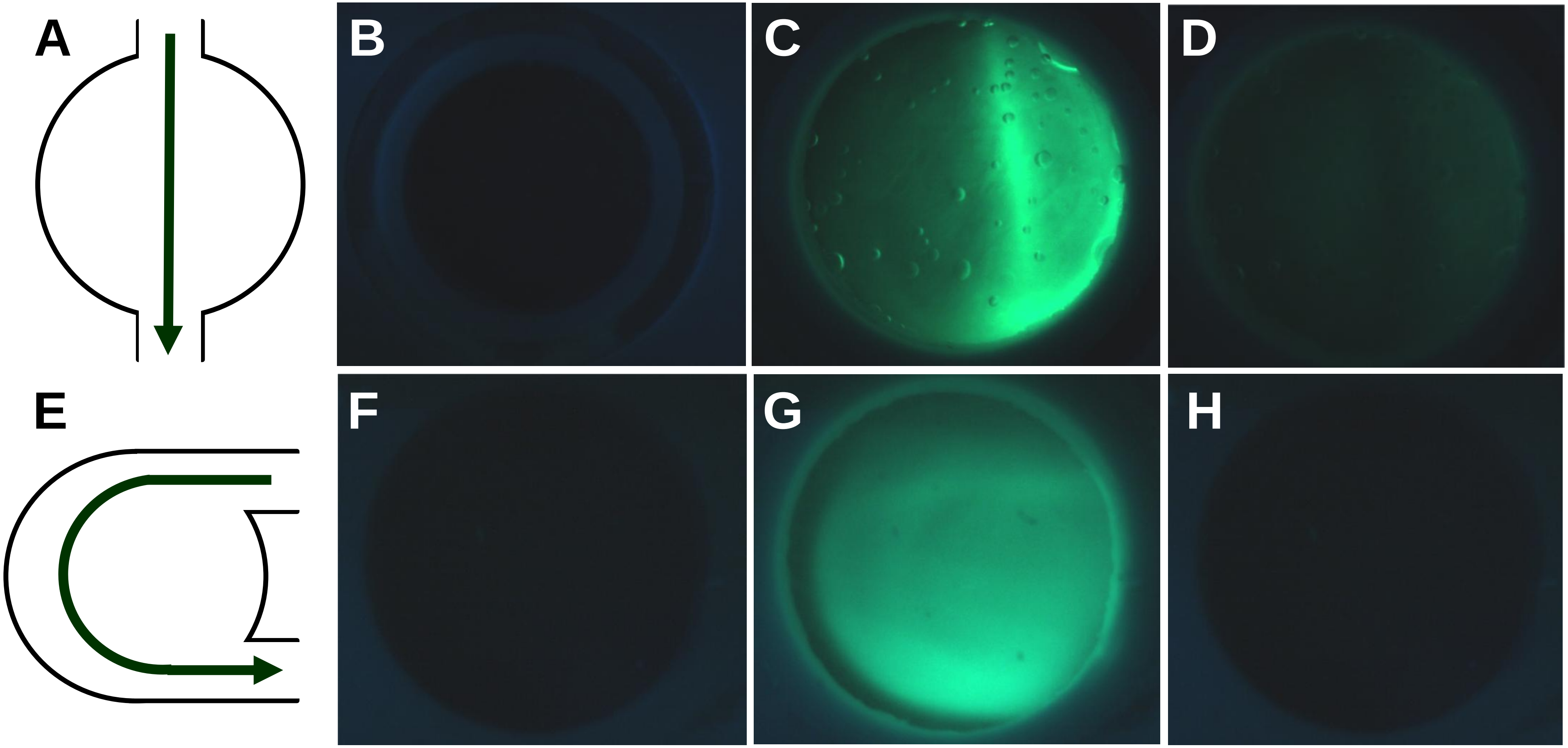

Figure 5

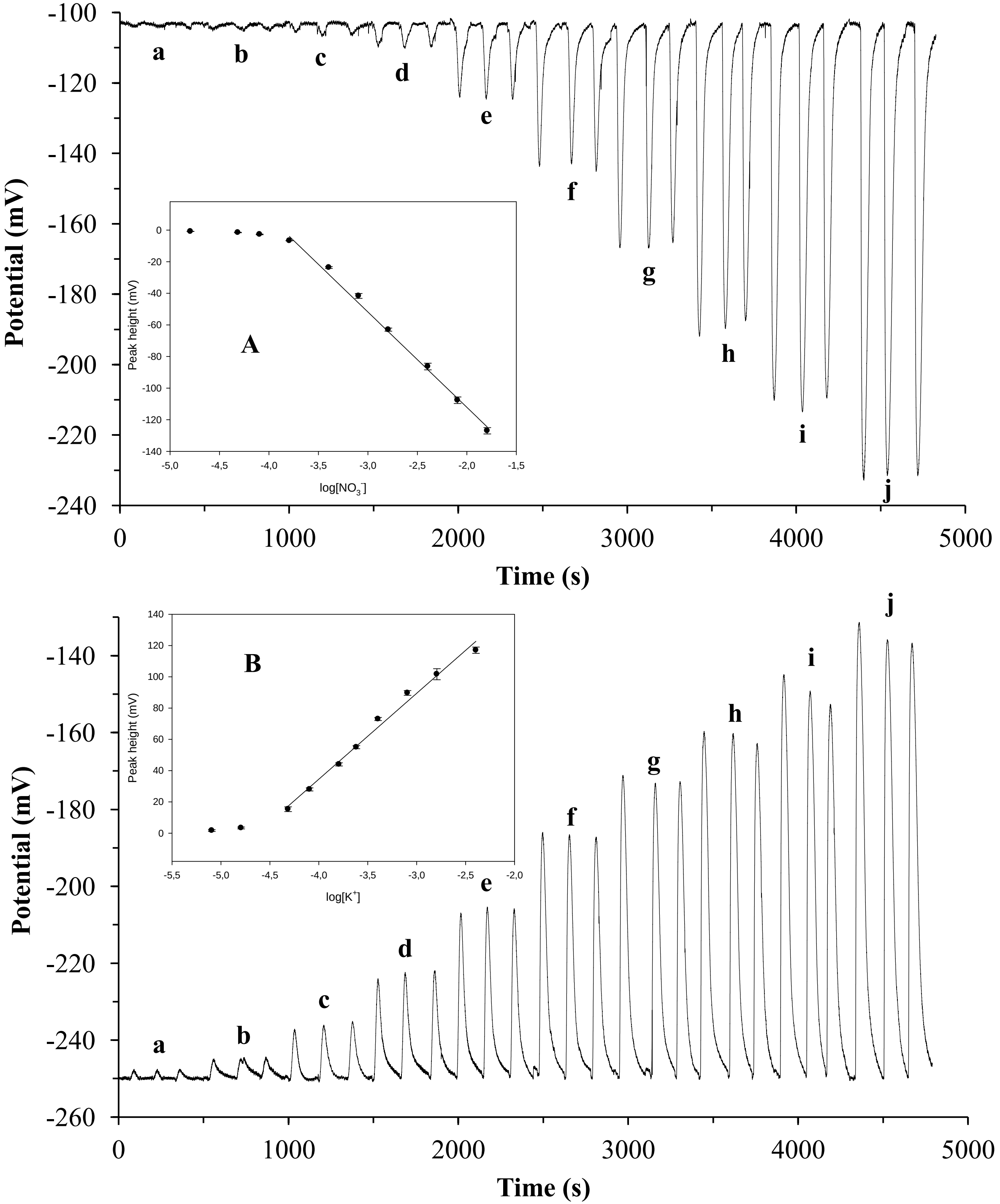
Potential (mV)
-100
-120
-140
-160
-180
-200
-220
-240
0
1000
2000
3000
4000
5000
Time (s)
a
b
c
d
e
f
g
h
i
j
A
Peak height (mV)
0
-20
-40
-60
-80
-100
-120
-140
-5,0
-4,5
-4,0
-3,5
-3,0
-2,5
-2,0
-1,5
log[NO$_3^-$]
Potential (mV)
-140
-160
-180
-200
-220
-240
-260
0
1000
2000
3000
4000
5000
Time (s)
a
b
c
d
e
f
g
h
i
j
B
Peak height (mV)
140
120
100
80
60
40
20
0
-5,5
-5,0
-4,5
-4,0
-3,5
-3,0
-2,5
-2,0
log[K$^+$]

Figure 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.

Figure 2. **A:** Layout of the biparametric prototype; **B:** Picture of the final constructed device; **a)** Fluidic connections; **b)** Electrical connectors; **c)** Detection chamber sealed with glued glass with the polymeric membranes inside; **C:** Front view of the detection chamber scheme; **1)** Ceramic layers; **2)** Polymeric membrane; **3)** Position of the microfluidic channel; **4)** Epoxy-graphite composite as transducer; **5)** Cover glass. **D:** Top view of the detection chamber scheme; **1)** Ceramic layer; **2)** Epoxy-graphite composite and polymeric membrane; **3)** Microfluidic channel.

Figure 3. Schematic diagram of microfluidics, detection system and experimental set-up. **a)** KCl 0.1 M auxiliary solution (**b)** 0.05 M Na_2SO_4 conditioning solution at pH 3; **c)** H_2O as carrier solution; **d)** sample; **P)** peristaltic pump; **V)** six-port injection valve; **W)** waste outlets; **1)** electrical connectors; **2)** reference electrode; **3)** working electrodes.

Figure 4. Sequence of images of the experiment conducted to compare the fluid dynamics inside the detection chambers using as sample of fluorescein (injection volume of 25 µL) and water as carrier solution (flow rate of 0.8 ml min^{-1}). The upper row shows the linear configuration **A)** and images at different times from the injection of the sample **B)** 0 s; **C)** 5 s and **D)** 20 s. The bottom row shows the circular configuration **E)** and the images at the same time from the injection of the sample **F)** 0 s; **G)** 5 s and **H)** 20 s.

Figure 5. Signal recording and obtained calibration curves for the microanalyzer calibration using KNO_3 standard solutions. (**A**) Nitrate electrode, NO_3^- solutions of 1 mg L^{-1} (**a**), 3 mg L^{-1} (**b**), 5 mg L^{-1} (**c**), 10 mg L^{-1} (**d**), 25 mg L^{-1} (**e**), 50 mg L^{-1} (**f**), 100 mg L^{-1} (**g**), 250 mg L^{-1} (**h**), 500 mg L^{-1} (**i**) and 1000 mg L^{-1} (**j**). (**B**) Potassium electrode, K^+ solutions of 0.3 mg L^{-1} (**a**), 0.6 mg

L^{-1} (**b**), 1.9 mg L^{-1} (**c**), 3.2 mg L^{-1} (**d**), 6.3 mg L^{-1} (**e**), 9.5 mg L^{-1} (**f**), 15.8 mg L^{-1} (**g**), 32 mg L^{-1} (**h**), 63 mg L^{-1} (**i**) and 155 mg L^{-1} (**j**).