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Integration of a sensitive carbon nanotube composite electrode in a ceramic microanalyzer for the amperometric determination of free chlorine

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Abstract

In this paper we report a green tape ceramic microfluidic analyzer that integrates a complete amperometric detection system based on a highly sensitive carbon nanotube composite electrode. As a proof of the integration concept, reference and counter electrodes were embedded into the microanalyzer body during the fabrication process. In order to increase the system functionality, and taking advantage of the surface renewability associated to composite electrodes, the working electrode was integrated in an exchangeable configuration. The microanalyzer was automated by means of the multicommutation technique, which allowed its autocalibration by the on-line preparation of standard solutions from a unique stock solution. The system was applied to the analysis of free chlorine in water samples. A noticeable low detection limit (0.05 mg L^{-1}) and a high-term stability were observed. To demonstrate the potentiality of this approach, in terms of analytical performance, it was also applied to the analysis of real samples obtained from a public swimming pool. The system characteristics make it ideal for unattended applications where the minimum user interaction and the maximum analyzer autonomy are required.

Keywords

carbon nanotube composite, amperometric sensor, chlorine, microanalyzer, green tape ceramics

1. Introduction

Over the past decade, research fields which focus on chemical production, pharmaceutical screening, drug investigation, medical diagnostics and environmental analysis have increased their interest in rapid and on-line determinations of low sample concentrations [1, 2] that complex samples usually contain. Recently, the emergence of new nano-materials has allowed the development of analytical sensors and detection systems capable of addressing these needs. The integration of electrochemical transducers based on nanostructures developed using new generation materials with high-tech microfluidic systems allows the production of chemical microanalyzers with a high analytical potential in a reduced space. In addition to reduced reagent consumption, shorter analysis time and reduced maintenance and fabrication costs, these kinds of systems also provide portability and are able to produce on-line information with temporal and spatial resolution.

Glass, silicon [3,4], polymers [5-7] and green tape ceramics [8-11] are the materials of choice for miniaturization purposes. Amongst all of them, the green tape technology presents some advantages when compared to the rest. Unlike glass or silicon, its fabrication process is simpler, cheaper and faster, since it does not require tedious and expensive conditions such as clean room facilities or specialized staff. Unlike the majority of polymers, green tape ceramics are highly hermetic and can withstand a wide variety of chemicals reagents [12]. Furthermore, its multilayer production approach easily allows the production of complex three-dimensional structures and the integration of additional materials compatible with the fabrication conditions, such as resins and some metals (i.e. silver, platinum). In addition, its compatibility with the thick-film technology permits the integration of screen-printed conductors to define electrodes or electronic circuits [13, 14]. Additional elements that are not compatible with the

fabrication process can be easily integrated once the device is bourn-out. Therefore, predefined holes to place these elements should be included in the design whilst taking into account the ceramics shrinkage which is totally predictable. The set of advantages associated to the green tape technology enables the development of highly integrated analyzers that can incorporate several stages of the classical analytical procedure [15-18].

Independently of the miniaturization technology applied to develop chemical microanalyzers, the detection system constitutes a main challenge, since highly sensitive techniques are needed as a consequence of the scaling-down of the flow system and the reduction of sample volumes. Optical and electrochemical detection systems are the most commonly used [19, 20]. Despite the high sensitivity presented by optical systems, their miniaturization involves the reduction of the optical pathway and, consequently, a decrease of their sensitivity. On the other hand, the high selectivity, sensitivity and the simple implementation of electrochemical methods, mainly voltamperometric, along with how well these devices maintain their analytical features during the scaling-down process compared with the optical methods, have contributed to their application in analytical microsystems. Therefore, miniaturized devices that integrate voltamperometric detectors can be frequently found in the literature [21, 22]. The performance of the electrochemical detection system is highly influenced by the nature of the material used as working electrode. This electrode should provide not only a favorable signal to noise ratio but also a reproducible response. Different kinds of materials, such as gold, platinum and different allotropic forms of carbon, have been found to be useful for electrochemical determinations in microfluidic devices [23-25]. Among all of them, carbon nanotubes (CNTs) [26-33] have been widely employed as electrode material for sensing different electroactives compounds due to their

remarkable mechanical and electrical properties [34-38]. Despite the electrochemical advantages provided by these materials as sensors, papers that deal with their integration in microfluidic devices are scarce in the literature. The first microchip integrating CNTs as sensor was reported by Wang et al. [39]. This microchip was applied to determine different standard analytes in a non-continuous flow mode using the amperometric technique. The device consisted of an exchangeable screen printed carbon electrode (SPE) modified with CNT/Nafion and integrated in a commercial glass CE (capillary electrophoresis) microchip by means of two adjustable pieces of methacrylate. Many other works reported in the literature are based on the same configuration [40-42]. Even though all these devices provided favorable results, it is important to notice that their configurations are based on the same commercially available microfluidic chip, which is modular integrated with the detection system. To obtain more robust analyzers, the monolithic integration of all platforms is desired.

Karuwan et al. [43] reported a microfluidic system based on PDMS and glass. The microfluidic channels were fabricated on the PDMS substrate using standard photolithography techniques. The detection system was fabricated on a glass substrate, later integrated to the fluidic platform, where Pt and Ag electrodes were deposited by sputtering. The working electrode consisted on CNTs grown using chemical vapor deposition (CVD). Although the system was satisfactorily applied to determine salbutamol, the fabrication of the chip involved a complex process, increasing fabrication costs. Moreover, once the electrode began folding, the chip became useless. To increase the versatility and reduce costs, an exchangeable detector is required.

This work deals, for the first time, with the integration of a CNT composite electrode into a green tape ceramic microfluidic device for amperometric determinations. This optimized CNT composite electrode is highly sensitive, not only due to the integrated

CNTs but also because of previous exhaustive characterization and optimization processes carried out [44]. Moreover, it was previously demonstrated that its analytical characteristics are comparable to those obtained using conventional electrodes based of gold and platinum [45]. To increase the microanalyzer functionality, the CNT-based electrode was integrated in an exchangeable configuration. This way, its surface could be renewed whenever needed.

This way, we have combined the excellent physical and electrochemical properties of CNT composite materials (high mechanical resistance and electrochemical sensitivity, as well as high signal to noise ratio, fast response, simple fabrication and low cost) with the advantages provided by the miniaturization concept, to develop an autonomous microanalyzer for real environmental applications. As a proof of concept, the microanalyzer was characterized and automated, by means of multicommutation techniques [4, 46, 47], to determine free chlorine in water samples. To evaluate the benefits of using this approach, in terms of analytical performance, it was applied to the analysis of free chlorine in real samples obtained from a public swimming pool.

2. Experimental

2.1 *Devices and apparatus*

Dupont 951 green tapes (thickness of 254 μm) were used as substrate for the fabrication of the multilayer microanalyzer. The process followed for the construction of the microanalyzer was that depicted in the bibliography [8]. The device layout, designed using computer assisted design (CAD) software, consisted on eight different layers as shown in figure 1A, being **a** and **h** the top and bottom layer, respectively. Layers **c, d** and **e**, once overlapped, compose a three dimensional mixer. The length of the mixer is a predefined parameter since once the device is fabricated, it cannot be modified. Due to

the influence of this parameter in the sample dispersion, two microanalyzers with different mixer lengths were fabricated to find out the optimal configuration for our application. The first device (D1) was designed with a mixer length of 203 mm; while the second one (D2) had a shorter mixer length of 108 mm.

Layers **f** and **g** constitute the structure designed to integrate a platinum disk acting as counter electrode as part of the amperometric detection system embedded in the device. Circular cavities included in layers **a**, **b** and **e** allow the later integration (after sinterization) of an exchangeable composite based working electrode. A total amount of 13 layers were used: 2x**a**, 2x**b**, 2x**c**, 1x**d**, 2x**e**, 1x**f**, 1x**g** and 2x**h**. Individual mechanization of layers was performed using a ProtoLaser200 machine (LPKF Laser & Electronics, Germany). The counter electrode consisted of a 4.8 x 4.6 x 0.125 mm platinum disk embedded in the ceramic device and sealed with sinterable glass paste (Dupont 9615). The reference electrode consisted in an Ag-based path (Dupont 6142) printed under an auxiliary channel (see figure 1B-k) through which a 0.2 M KCl solution flow constantly to maintain stable the applied potential [16]. Electrical contact between the embedded electrodes and an external electronic set up was established by means of screen printed patterns (Dupont 6146) and an external connector soldered to the ceramic body after sinterization (see figure 2B).

Once burned-out, according to the predictable ceramic shrinkage, the final devices (see figure 1B) presented an inner total volume of 470 µL and 250 µL for D1 and D2, respectively. Both present an inner-channel with dimensions of 1.9 mm width and 400 µm height. The working electrode was separately prepared and integrated once the device was sinterized. The sensitive active area of the composite electrode (4 mm^2) was limited by the dimension of the hole located above the main flow channel in the working electrode cavity (see figure 1B-i).

The composite based mixture for the working electrode fabrication (see figure 2A) was prepared by mixing polymer EpoTek H77A and its corresponding hardener (EpoTeK H77B) in a 20:3 (w/w) ratio and using a previously optimized composition of 10% of multiwall carbon nanotubes (MWCNTs) [44]. The composite mixture was homogenized during 60 min. For the electrode construction, the composite mixture was placed into a PVC fitting (Cavro, 4mm i.d, 15mm length), containing a cooper disk (2 mm diameter) soldered to a 2 mm banana male end connector. The male connector was used as electrical contact with the external electronic set up. The final dimensions of the cavity to be filled by the CNT composite were 2mm in depth and 4mm in diameter. The working electrode was integrated to the microanalyzer by means of a PVC nut previously glued to the ceramic body over its main flow channel, in a cavity specifically designed for this purpose. This nut was placed in the green tape ceramic device after it was burnt-out. Final sealing between the nut and the device was achieved with Araldite resin. The configuration used for the working electrode, using the PVC body electrode as the external connector, allowed the improvement of the system robustness by avoiding any liquid leakages that may interfere the electrical measurements. Figure 2B presents one of the ceramic devices fabricated.

Amperometric measurements were performed using a commercial amperimeter LC-4C (Bio Analytical Systems Inc, West Lafayette, IN, USA.), connected to a personal computer by means of a data acquisition card ADC-42 PicoTechnology (Pico Technology Limited, St. Neots, Cambridgeshire, UK) for data registering and visualization. The experimental set up of the complete flow analysis system is depicted in figure 3. The manifold includes a three-way solenoid valve (NResearch 161T031, NResearch Incorporated, West Caldwell, NJ, USA), controlled by a virtual instrument especially developed to define a multicommutation function [48], and a four-channel

peristaltic pump (Gilson Company, Inc., Columbus, OH, USA) for liquid pumping. Silicon tubing, with a 1.14 mm internal diameter (Elkay Products) and 0.7 mm internal diameter Teflon tubing (Omnifit) completed the flow system.

2.2 *Chemicals and Reagents*

L-purified multiwall carbon nanotubes prepared using the chemical vapor deposition process (MWCNTs purity > 95%, length 5-15 μm, outer diameter 10-30 nm) were purchased from SES Research (Houston, TX, USA). Resin epotek H77 and its corresponding hardener which was supplied from Epoxy Technology (Billerica, MA, USA) were used as polymeric matrix. All solutions were prepared using deionized water from a Milli-Q system (Millipore, Billerica, MA, USA). Sodium hypochlorite (10-13%), potassium dihydrogen phosphate (99.5%) and potassium chloride (99.5%) with the highest quality grade available, were obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.4 *Analytical performance*

Chlorine analyses in the microanalyzer were carried out at a set potential of -100 mV (*vs* Ag/AgCl). The flow hydrodynamics parameters, such as the flow rate and injection volume, were optimized using a 1 mg L^{-1} standard solution off-line prepared. Different times for the valve activation (on/off), without multi-commutating, were fitted to dispense the injection volume required for every flow rate evaluated during optimization.

The analytical response for chlorine was evaluated using different standard solutions in different concentration ranges. Standard solutions were on-line prepared from one stock

solution (5 mg L^{-1} of chlorine) by means of a multicommutation technique that allow the autocalibration and automatic analysis of samples.

In general, this technique is applied in continuous flow systems by means of the use of discrete commutation devices (three-way solenoid valve). The preset of different frequencies of valve commutation (on/off), combined with a constant flow rate, allow us to create sequences of deionized water/stock solution (binary sampling in tandem configuration) of n aliquots which interpenetrate themselves, producing the dilution needed for each different standard concentration. The injection volume is controlled by measuring the time that the deionized water/stock solution or sample flows through the system.

In fact, here the different standard solutions were prepared by means of different duty cycles applied to the digital signal that controls the commutation system. The overall commutation binary time was 15s and the mixing ratios (deionized water/stock solution) to obtain the desired concentrations were 0.8/0.2 s, 0.6/0.4 s, 0.4/0.6 s, 0.2/0.8 s, etc. Using these ratios, the stock solution was diluted 20, 40, 60, 80%, etc. The minimum commutation time that provides a reproducible signal was 0.1 s.

The standard solutions prepared on-line and the samples, were pre-treated and diluted (1:1) in a 0.2 M phosphate buffer solution and a 0.2 M KCl at pH 5.5 into the microanalyzer prior to the detection cell [45]. This pre-treatment step allows adjusting the ionic force and pH of the standard solution/sample, before being analyzed.

Regarding the real sample analysis, a total of twenty samples were analyzed. Thirteen of them were collected from a swimming pool located in the sport facilities of the Universitat Autònoma de Barcelona (UAB). Five doped samples were prepared by dilution of the stock solution in real samples. Two synthetic samples, used as control, were prepared by dilution of the stock solution in deionized water. Samples were

simultaneously analyzed using the microanalyzers proposed and the standard N,N-diethyl-p-phenylenediamine (DPD) colorimetric method [49], which consists in a Kit-commercial colorimeter (HACH, Düsseldorf, Germany) that provides measurements directly in mg $L^{-1}$of free chlorine.

3. Results and discussion

The main goal of this study was the development of a highly integrated and sensitive microanalyzer able to operate during a considerable period of time, providing long-term stability signals, and under unattended conditions. The microanalyzer integrates a complete amperometric detection system based on a highly sensitive CNT composite electrode [44]. To automate the calibration and analysis processes, it was coupled to a multicommutation system. This approach allowed us to overcome some drawbacks usually presented by its counterpart in the macro scale (lack of portability, reagents consumption, maintenance and fabrication costs, etc.) [45].

The optimum working potential, -100 mV, was selected on the basis of previous results obtained using CNT composite electrodes for chlorine determination [45]. The first experiments were aimed to optimize the flow hydrodynamic parameters, such as the injection volume, flow rate and mixer length. For this purpose, an experimental face centered cube design that included eleven experiments was applied for a standard solution of 1 mg L^{-1} of free chlorine. This concentration corresponds to an intermediate value within the legal concentration range established by the current Spanish legislation for free chlorine in swimming pool water. Such a range is usually found between 0.5 and 2 mg·L^{-1} [50]. The injection volume was evaluated in a range between 50 and 200 µL. The minimum affordable value of this interval is defined by the sensor sensitivity, while the maximum value is limited by the device dimensions. For this experimental

design, it was agreed to avoid that the maximum injection volume exceeded the 80% of the total inner volume of device D2 (device with smaller inner volume, 250 µL). On the other hand, the flow rate was studied between 0.4 and 1.2 mL min^{-1}. This interval was selected considering the system response time as well as the reagents consumption.

As expected, results showed an increase of the peak height as the injection volume increases. Figure 4 depicts how the peak height and width changes for different flow rates and mixing reactor lengths. It can observed that, for both devices, the peak height was influenced by the flow rate, providing higher signal for a flow rate of 1.2 ml min^{-1} (lower sample dispersion). Nevertheless, for the shorter mixing reactor (D2), higher signals and smaller analysis times were obtained. It is known that different parameters, such as the mixer length, diameter and section of the channel, among others, [51] affect the dispersion coefficient of the microfluidic system. In this study, all of these parameters, except for the mixer length, were maintained constant for both devices.

Taking into account that the main purpose of this optimization was to find out the experimental conditions that provide the maximal analytical signal with the highest analytical frequency and minimum reagents consumption, the device with shorter mixing reactor (D2) was chosen to continue this study. Moreover, the optimum hydrodynamic parameters were set at 200 µL for injection volume and 0.8 mL min^{-1} for flow rate. The flow rate was chosen according to the values predicted by the contour plot during the experimental design (result not showed). Even though the maximum analytical signal was obtain for the maximum flow rate evaluated (1.2 mL min^{-1}), 0.8 mL min^{-1} was chosen as the optimum value since it allowed reducing the reagent consumption without punishing significantly the peak high signal (see figure 4, red dotted line).

In these conditions, the analysis time for each sample was found to be 70 s (time from injection to steady-state signal). Using device D2, a later experiment was focused on evaluating the analytical response of the system to changes in the concentration of chlorine. A linear relationship between the chlorine concentration and the cathodic peak height current was observed for different concentration ranges. One range expands from 0.2 to 4 mg L^{-1}, being the sensitivity -0.046 (±0.001) µA L mg^{-1}. The measurements were carried out by triplicate and a 95% of confidence level (see figure 5). The limit of detection (LOD) was estimated using the signal to noise (S/N = 3) criterion [52]. Under these conditions, a LOD of 0.05 mg L^{-1} was achieved. This concentration range is suitable for monitoring free chlorine in swimming pool waters given that this range contains the minimum and maximum legal chlorine concentration allowed by the current Spanish legislation in swimming-pool waters [50]. In order to gain more insight about the analytical response of the system, chlorine concentrations higher than 4 mg L^{-1} were also evaluated. A wider linear response was obtained for concentrations in the range from 3 to 60 mg L^{-1}, with a sensitivity of -0.042 (±0.005) µA L mg^{-1}. The measurements were carried out by triplicate using a 95% confidence level. These results showed that the system responds lineally in all the evaluated concentration ranges. Higher concentrations up to 160 mg L^{-1} showed the same linear response (not presented in this work).

In order to evaluate the analytical response of the microanalyzer, in terms of repeatability of the signal, a 3.7 mg L^{-1} free chlorine standard solution was used. A RSD of 4% was obtained for 50 replicates performed consecutively, obtaining an average peak current value of -0.145(±0.002) µA. The repeatability of the signal was also evaluated for a 1 mg L^{-1} free chlorine standard solution. The result showed a RSD of 5% with a mean average peak (n=50) current value of -0.0253 (±0.0004) µA. As

expected, a slightly lower value of repeatability for the lowest concentration was obtained. Nevertheless, a good repeatability for both concentrations was demonstrated.

In order to make an estimation of the loss of sensitivity, multiple calibration experiments were carried out with the ceramic microanalyzer during several days. A loss of sensitivity of a 30% compared to its initial value was observed after 300 analyses. During this period, the sensor was kept in the microanalyzer without renewing its surface. Regarding these results, a simple surface pretreatment step, without disassembling the sensor, was applied to increase the sensor sensitivity and extend its lifetime. This pretreatment consisted of applying, before each calibration, a 1.2 V fix potential during 30s. The results showed that the sensitivity was recovered up to a 97% of its initial value. This pretreatment allows us to increase the sensor lifetime for at least ten days without having to disassemble it from the microsystem to renew its surface.

The analytical characteristics achieved by the integration of an exchangeable highly sensitive CNT electrode into an automated ceramic microanalyzer, in terms of linear range and reproducibility, allowed its application to the analysis of real samples, which has not been presented by similar devices previously reported [18].

3.1 *Real sample analysis*

A total of twenty samples were analyzed with the developed microanalyzer during several days. Thirteen samples were directly collected from a public swimming pool and five more were doped with a chlorine standard solution after collected. Finally, two samples were synthetically prepared and used as control. Table 1 shows the analytical results obtained with both methods and the recovery value. Statistical paired t-test and the least-square linear regression were used to make the statistical evaluation of the method. No significant differences were observed at 95% confidence level. In paired t-

test: $t_{cal} = 1.782 < t_{tab} = 2.093$, while in the least square linear regression the slope and intercept were 1.06±0.06 and -0.04±0.05, respectively (r^2 =0.99; n= 20; 95% confidence level).

4. Conclusions

An optimized multiwall carbon nanotube composite electrode has been successfully integrated in an amperometric microanalyzer based on the green tape ceramics technology. The miniaturized analyzer, combining the excellent properties provided for the ceramic technology and the well-known properties of CNT composite electrodes, was used for the analysis of free chlorine at very low concentrations in real samples. Continuous monitoring of the analyte was possible, during considerable periods of time without changing or renewing the electrode surface, by means of a simple pretreatment step, consisting on applying a fix potential of 1.2 V during 30 s before its use in new analysis. This pretreatment allowed us to increase the sensor lifetime for at least ten extra days. In addition, the exchangeable configuration of the working electrode allows its exchange whenever is necessary without having to rebuild the complete device. Moreover, since CNT composite electrodes surfaces can be renewed by a simple polishing, this exchangeable configuration also allows the sensor regeneration at any desired. Regarding to the real samples analysis, an excellent agreement between the obtained results with the proposed system and the standard method for free chlorine determination was achieved. This demonstrates the high potential of the ceramic microanalyzer integrating a CNT optimized composite electrode for measurements at low concentrations, matching the actual legal requirements of free chlorine in swimming pool waters.

Taking advantage of the green tape technology, further work can be performed to increase the integration level of the current microanalyzer, by the monolithic integration of electronics and microactuators, to obtain an autonomous and portable device to be used in-the-field environmental applications with the possibility of providing in-time and *in-situ* information under unattended conditions.

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Figure and table captions

Figure 1 (A) Layer by layer layout of device D2: a) upper layer, b) reagents/sample inlet/outlet, c, d and e) mixer layers, f and g) Pt counter electrode integration, h) bottom layer. (B) Fluidic distribution: i) working electrode cavity, j) Pt counter electrode, k) reference electrode, l) mixer

Figure 2 (A) CNT composite-based working electrode. (B) Amperometric microanalyzer integrating CNT composite electrode. External connection of: 1) reference electrode, 2) counter electrode and 3) working electrode

Figure 3 Experimental manifold used for chlorine determination in the ceramic microanalyzer based on CNT composite amperometric sensor. (a) Sample or stock solution; (b) deionized water; (c) carrier solution; (d) 0.2M KCl; (e) waste; (f) solenoid valve and (g) pump

Figure 4 Shows the influence of the flow rate and the mixing reactor length on the analytical signal, for a 1 mg L^{-1} of free chlorine standard solution and 200 µL of injection volume. In this figure, D1 and D2 correspond to the microanalyzers fabricated considering different total inner volume (D1: 470 µL and D2: 250 µL). The red dotted line shows the analytical signal obtained using the chosen optimum parameters, for a concentration of 1 mg L^{-1}

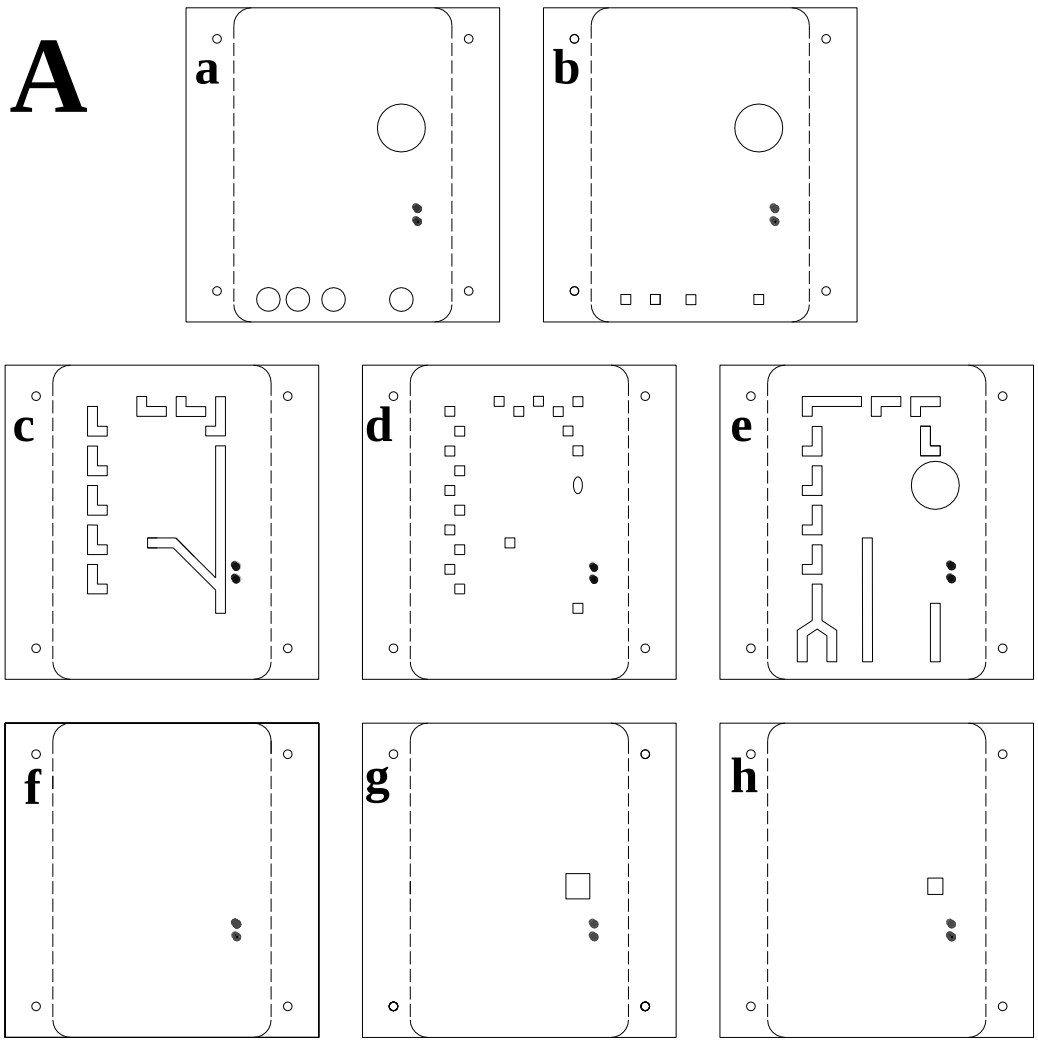
Figure 5 Ceramic microanalyzer (device D2) response for free chlorine concentrations from 4 to 0.2 mg L^{-1}. The inset depicts a calibration curve corresponding to the amperometric record (slope -0.045(±0.004), intercept 0.012 (±0.008), r^2= 0.996)

Table 1 Free chlorine analysis in swimming pool water samples with the microanalyzer as well as the DPD colorimetric standard method and the recovery value

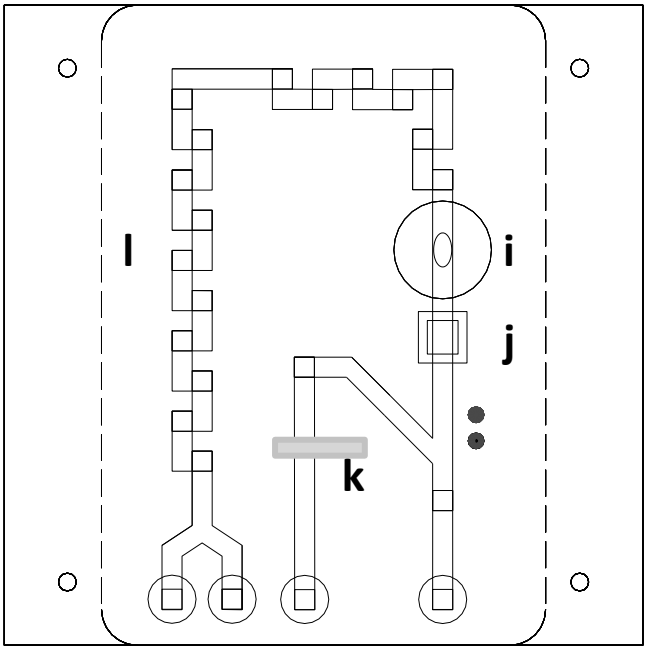
Table 1

Sample	Standard method ($mg \cdot L^{-1}$)	Microanalyzer ($mg \cdot L^{-1}$)	Recovery (%)
Swimming pool water			
1	0.63	0.60 (±0.06)	96
2	0.65	0.68(±0.01)	104
3	0.35	0.36(±0.03)	102
4	0.46	0.48(±0.03)	105
5	0.79	0.77(±0.05)	98
6	1.01	1.01(±0.01)	100
7	1.14	1.23(±0.09)	108
8	1.07	0.97(±0.06)	91
9	0.5	0.49(±0.03)	98
10	0.91	0.96(±0.08)	105
11	0.96	1.01(±0.03)	105
12	1.02	1.03(±0.03)	101
13	0.92	0.90(±0.03)	98
Doped samples			
14	1.05	1.06(±0.03)	101
15	1.43	1.49(±0.06)	104
16	1.37	1.36(±0.03)	100
17	1.12	1.16(±0.01)	103
18	2.8	2.98(±0.06)	107
Control samples			
19	0.85	0.88(±0.01)	103
20	1.53	1.53(±0.03)	103

Figure 1



B



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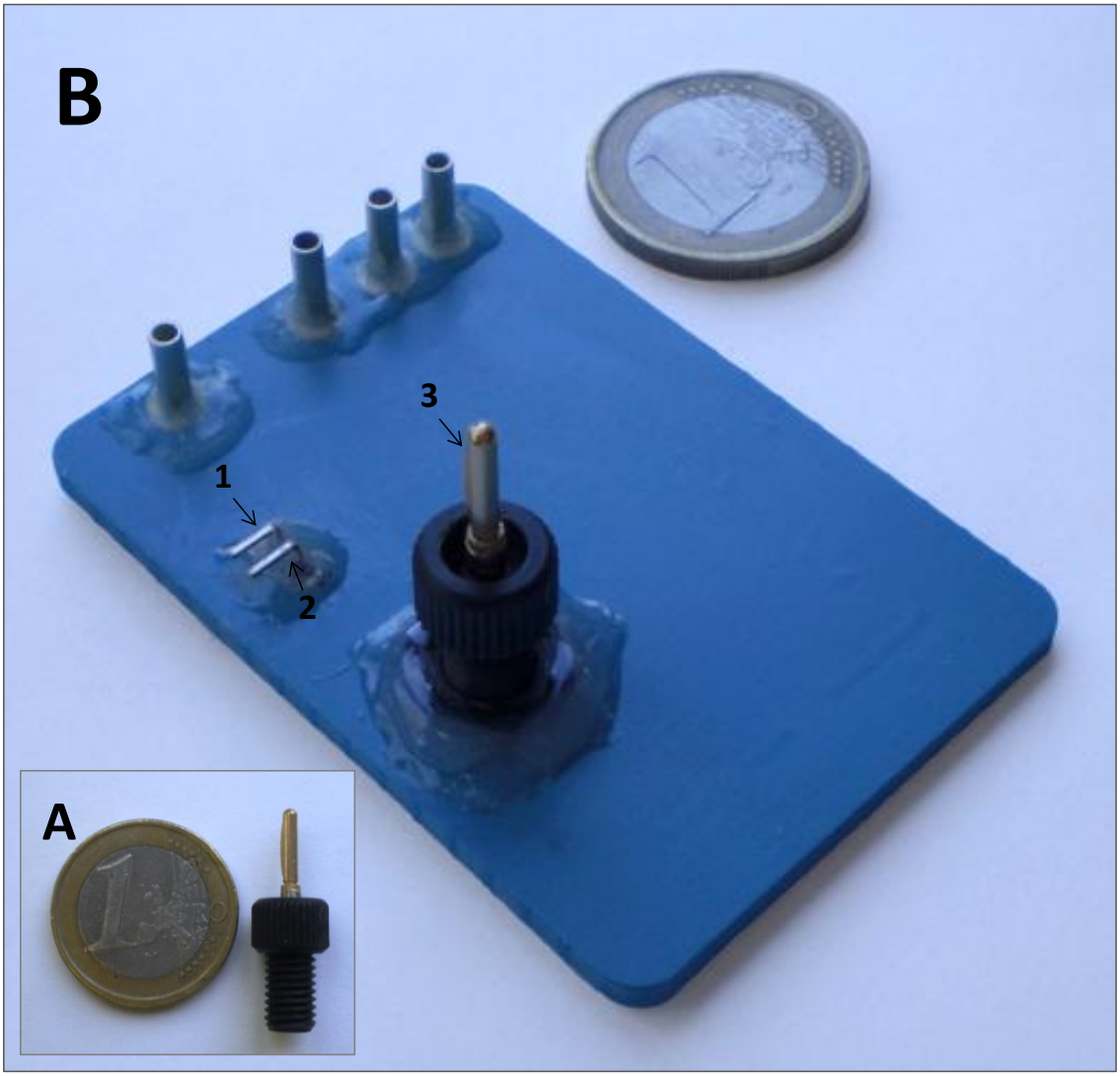

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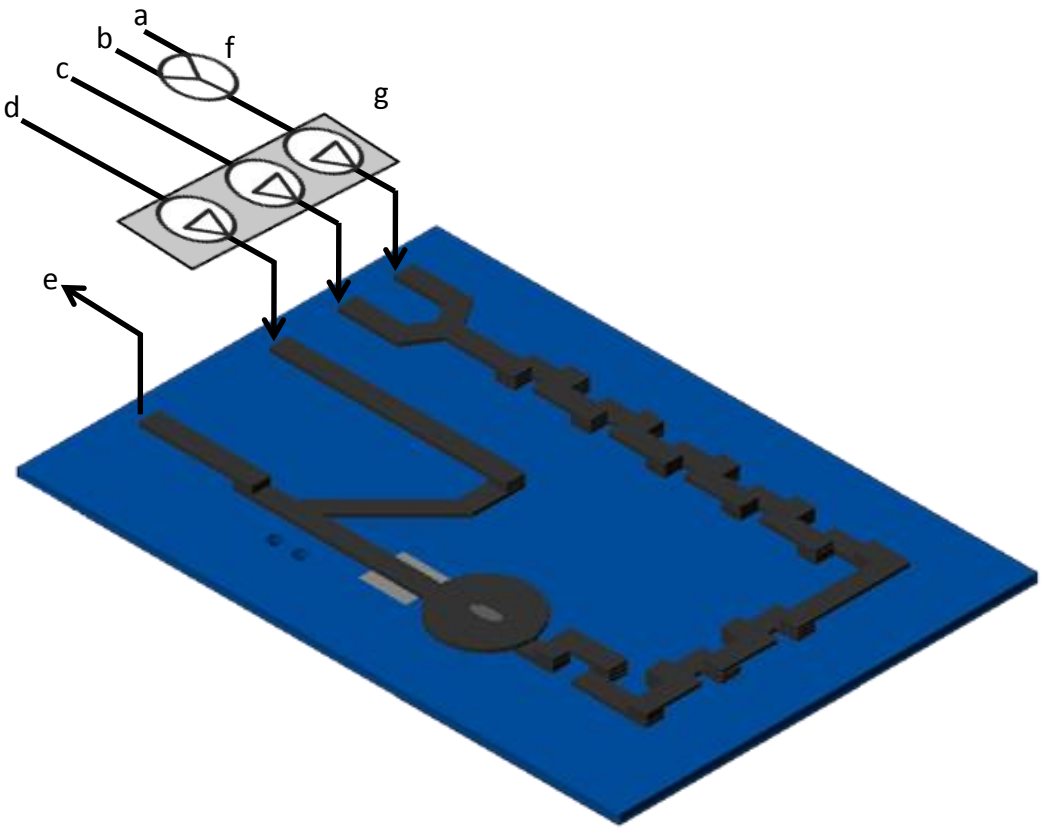


Figure 4

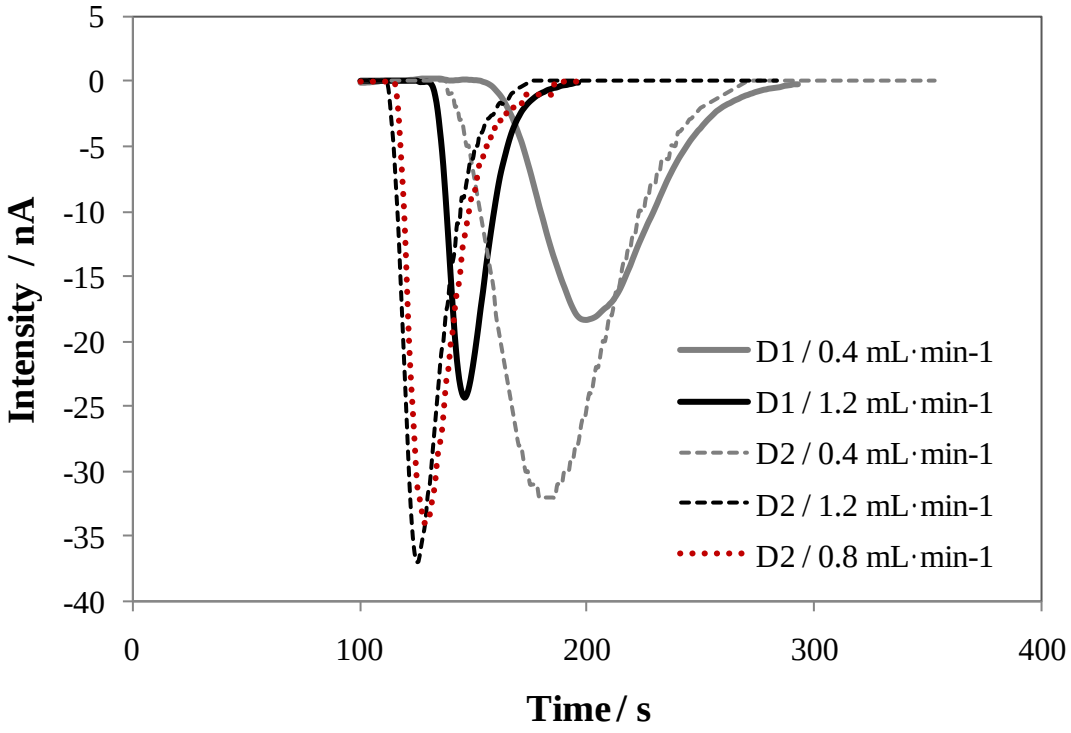
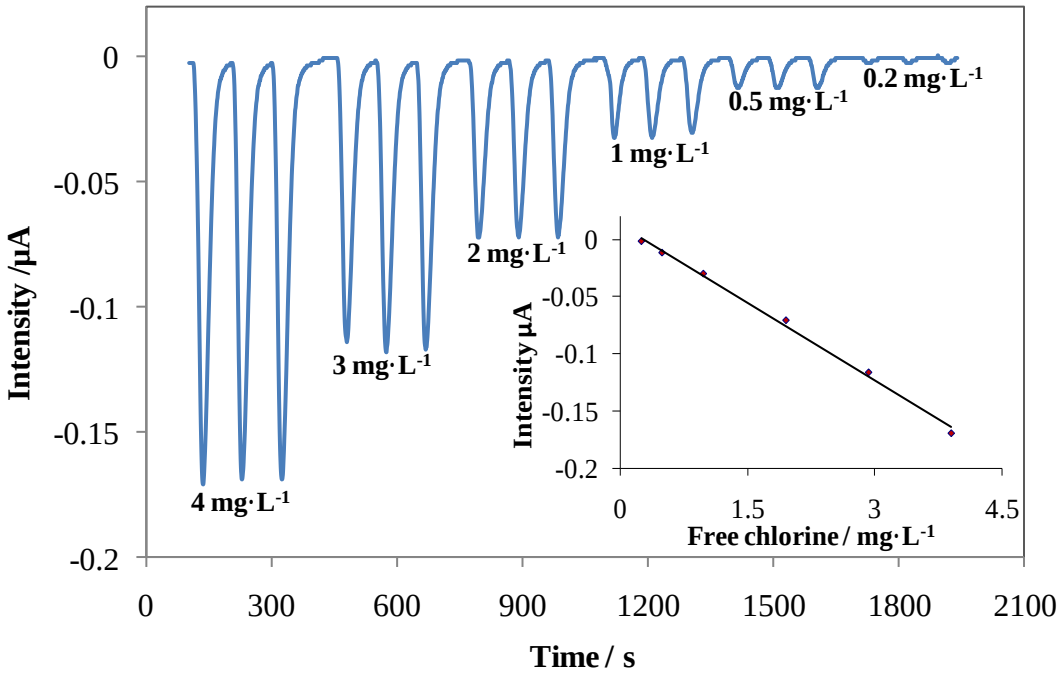

5
0
-5
-10
-15
-20
-25
-30
-35
-40
Intensity / nA
0
100
200
300
400
Time / s
D1 / 0.4 mL·min-1
D1 / 1.2 mL·min-1
D2 / 0.4 mL·min-1
D2 / 1.2 mL·min-1
D2 / 0.8 mL·min-1

Figure 5


0
-0.05
-0.1
-0.15
-0.2
Intensity /µA
0
300
600
900
1200
1500
1800
2100
Time / s
4 mg·L-1
3 mg·L-1
2 mg·L-1
1 mg·L-1
0.5 mg·L-1
0.2 mg·L-1
Intensity µA
0
1.5
3
4.5
Free chlorine / mg·L-1