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Credit author statement

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Electrochemical Micropipette-Tip for Low-Cost Environmental Applications: Determination of Anionic Surfactants through their Interaction with Methylene Blue

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Abstract

Miniaturization is one of the main requirements of the design of portable devices that allow in-field analysis. This is especially interesting in environmental monitoring, where the time of the sample-to-result process could be decreased considerably by approaching the analytical platforms to the sampling point. We employed traditional mass-produced and low-cost elements (micropipette tips and pins) in an out-of-box application to generate an innovative and cost-effective platform for analytical purposes. We have designed simple and easy-to-use electrochemical cells inside polypropylene micropipette tips with three stainless-steel pins acting as the working, reference and counter electrodes of a potentiostatic system. The pin acting as working electrode was previously coated with carbon ink, meanwhile the rest were used unmodified. In this way, electrochemical measurements were done directly in-the-tip using low volumes (µL) of sample. The devices showed good reproducibility, with a relative standard deviation of 7% (n=5) for five different tip-based complete electrochemical cells. As a proof-of-concept, its utility has been probed by the determination of an anionic surfactant (sodium dodecyl sulphate, SDS) in water through its interaction with methylene blue (MB). Two different alternatives were presented: 1) electrochemical determination of the MB remaining in the aqueous phase after extraction of the pair SDS-MB to an organic medium.

Keywords: micropipette-tip electrochemical cell, stainless-steel analysis, electrochemical analysis, water analysis, sodium dodecyl sulphate.

1. Introduction

The design of miniaturized and low-cost sensing devices is an area of enormous interest in the field of Analytical Chemistry. They are definitely required to move...
(bio)chemical analysis from the bench to the field [1]. In fact, the combination of
wireless sensors with smartphones is producing platforms well suited to perform
decentralized analysis [2,3]. In this context, the electrochemical detection must be
pointed out since it is low cost and easily miniaturized and provide high selective and
sensitive methodologies [4].

In terms of cost-effectiveness, the use of common elements for out-of-box
applications is clearly increasing. They are already mass-produced items that can be
utilized for novel applications. In 2016, Whiteside’s group introduced the use of
stainless-steel pins as electrodes in combination with thread for microfluidic
determination of lactate [5]. The modification of these metallic elements with carbon ink
allowed their use to determine glucose enzymatically, in static [6] and flow-based
systems [7]. Batch injection analysis has also been demonstrated for epinephrine
determination using pin-based cells [8]. Their low size enabled the design of arrays for
performing simultaneous measurements using a multichannel potentiostat [6].
Similarly, other mass-produced elements of common use such as staples have been
modified for use as electrodes in new electrochemical low-cost platforms [9].

Among the items that are widely employed in most (bio)chemical laboratories and
can be employed in out-of-box applications are micropipette tips. They can be used for
different purposes apart from dispensing liquids, their main function. These novel
applications include sample purification as in the case of tips containing a bed of
chromatography media for the detection of human chorionic gonadotropin (hCG) and
prostate-specific antigen (PSA) in urine samples [10] or selective extraction, with
integrated molecularly-imprinted monoliths, of the toxin berberine [11] or the pesticide
methomyl [12]. More recently, our research group designed an enzymatic
immunoassay where the inner surface of a micropipette tip was turned into a capture
zone for anti-tissue transglutaminase (IgA) [13], antigen of interest for the detection of
the celiac disease.

Moving further in this direction, in this work we add a new functionality to this
common and affordable consumable material, easily found in laboratories. With this
aim, we have integrated a very simple electrochemical cell. Already in 1991, a
micropipette tip was used as a platform for the fabrication of carbon fiber
ultramicroelectrodes [14]. Following this idea of using the tip as container, miniaturized
electrochemical devices were designed using micropipette tips combined with e.g.,
graphite composite [15] or epoxy resin [16]. In these examples, the micropipette tip
acted as the body of the working electrode, that had to be immersed in the sample
solution for performing measurements, as happens with e.g., a polymeric cylinder that
encloses carbon paste or a pencil lead. The other two electrodes (reference and counter electrodes) had to be introduced in the solution as well, which could be done: i) independently, as different elements, or ii) integrated in the outer part or the tip. Apart from these approaches, the tips can be used, after sealing the bottom, as low-cost and low-volume electrochemical cells. Following this, three small-size electrodes with a pencil graphite working electrode were introduced in a tip-based cell [17]. However, in all these cases the tip is modified and cannot be used in combination with a micropipette for performing its original function: aspirating and dispensing solutions. There is a unique report on the use of a micropipette-tip used as container of a complete electrochemical cell [18] that retained this function. In this case, the sample was aspirated and analyzed thanks to the introduction of three wire electrodes (with gold-based working and reference electrodes) and a cotton wool filter (for medium storage and sample purification) inside the tip, in a new lab-on-a-tip approach for decentralized electroanalysis of Cu\(^{2+}\) in water.

In this work, we propose the use of a simpler and lower-cost device that employs stainless-steel pins as electrodes and integrates them in the micropipette tip, which becomes now multifunctional. A pin modified with carbon ink is used as working electrode, and two more pins, unmodified, are used as reference and counter electrodes. One important advantage is that the modification of pins with carbon ink allows their use in many applications. Carbon materials, such as carbon paste/ink and graphite, are widely used in electrochemistry because of their advantageous properties: carbon is cheap and chemically inert and shows high surface area and electrical conductivity, low background currents and a wide potential window [19,20]. The bottom of the tip has a diameter that allows the introduction of the pin covered with a thick film of carbon, with the head of the pin acting as stopper. Following this new design, the electrochemical cell can be fabricated in an extremely fast and reproducible way employing inexpensive materials.

Thus, we present here a modified micropipette tip that act as an electrochemical cell, very useful for in-field analysis. The combination of common (stainless-steel pins) and lab (micropipette tips) materials described here draw us to the idea of a simple “everywhere” electroanalysis that could be performed by non-qualified personal. The portability of the system makes it useful for environmental analysis, e.g. water and wastewater in situ analysis. Then, we decided to evaluate this new electrochemical lab-on-a-tip device for assessing the quality of water in terms of the presence of anionic surfactants. They mainly come from household aqueous discharge, industrial laundering and other cleansing operations. Surfactants are considered emerging
contaminants. They have negative effects on water quality since they tend to congregate providing properties such as foaming, emulsification and particle suspension. Moreover, surfactants can pass through wastewater treatment plants and reach environmental and even drinking water. These compounds produce harmful effects in aquatic flora and fauna, and also in human health [21]. Therefore, the concentration of surfactant in water is an important parameter to assess the water contamination and quality. In the United States, ionic surfactants (mostly anionic) are about two thirds of the total surfactants used [22]. The standard analytical method highlights anionic surfactants, such as sodium dodecyl sulphate (SDS), as the most common substances present in water and it is based in their methylene blue (MB) activity. Anionic surfactants interact with MB, a cationic dye, forming an ionic pair. This complex is transferred from the aqueous solution into an immiscible organic solvent upon equilibration. The blue color intensity obtained in the organic phase is measured spectrophotometrically and is proportional to the concentration of anionic surfactants. This interaction has been applied also inversely, to adsorb MB (dye discharged to the environment from textiles, dyeing and printing industries) on SDS-modified zeolites [23]. We have applied a modification of this standard analytical method in which a reduction in the sample volume and, henceforth, in the use of reagents is achieved [24].

Moreover, instead of using a colorimetric assay, we have taken advantage of the electrochemical activity of MB and its growing interest in biosensing (e.g. as indicator of DNA hybridization processes through its interaction with the double strand [25]). Then, we have adapted the modified standard method to detect electrochemically MB, directly in the micropipette tip, as a way of determining SDS, a MBAS (methylene blue active substances) frequently found in wastewaters. Then, when a constant concentration of MB is added to the sample, its residual concentration in the aqueous phase, after interaction with MBAS and further extraction to an organic media, is indicative of the initial MBAS concentration in the sample.

Additionally, and considering the influence of surfactants on carbon electrodes, which can improve electrochemical processes [26–28], a simplified electrochemical method for the determination of SDS without following the extraction protocol previously indicated, was also developed. In this way, an increment in the electrochemical signal of MB (fixed concentration), seen for increasing SDS concentrations, is the basis for its determination. Then, in this work, we report two simple alternatives for SDS determination in water samples using an innovative and low-cost multifunctional electrochemical platform.
2. Material and methods

2.1. Chemicals and materials

Through all this work, 100-1000 µL polypropylene micropipette tips were used (Labbox Labware). For the assembly of the system and to facilitate micropipette handling, a foot stand with a three-point gripper fastening tong was employed. As electrodes, 26 x 0.59 mm stainless-steel pins (Metalurgica Folch) were selected. Carbon paste (Gwent Group Ref. C10903P14) and N,N-dimethylformamide (DMF, Merck) were employed for the fabrication of the working electrode. Acidic solutions of different concentrations of methylene blue (Sigma Aldrich) were prepared in 0.5 M HCl (hydrochloric acid 37% from Merck). Working SDS solutions for optimization studies were prepared in ultrapure water. Also, chloroform (trichloromethane, Sigma-Aldrich) was used for the analysis of anionic surfactants. Millipore Direct-Q(R) 3 UV was used to obtain purified water.

2.2. Electrochemical “in-the-tip” cell design

We used stainless-steel pins as electrodes. The use of this kind of pins as electrodes has been reported previously [6,7], including the stability of a stainless-steel pin acting as reference electrode by comparison with a saturated calomel electrode (a variation not higher than 3 mV over 30 min). The various parts of the pins were used for different purposes, all of them schematized in Figure 1A. First of all, the stainless-steel pins used as working electrodes (WE) were modified with carbon ink. Carbon paste was diluted with N, N-dimethylformamide (50% w/w of carbon paste in DMF) to generate the carbon ink for the modification. The mixture was vortexed for a few seconds and then sonicated (37 kHz of frequency and 320 W of power) for 1 h. Stainless-steel pins were mass modified adhering them, by their head, to a piece of double-sided tape. Then, the stems were painted thrice with the carbon ink using a brush (Figure 1B). Between the two first coatings, the pins were introduced in the oven at 70°C for 15 min. After the last one, they were left for 1 h at 70°C.

Once the WEs were ready, two bare stainless-steel pins (one acting as reference electrode, RE, and the other one as counter electrode, CE) were inserted in the micropipette tip at a distance of 28 and 30 mm from the bottom, respectively. To favor this, the micropipette tip was previously introduced in the oven at 70°C for 2 min. After this, a volume of sample was aspirated, and the micropipette tip was sealed at the bottom by introducing a pin covered with carbon ink (the WE). This process is schematized in Figure 1C.
As the diameter of the pin stem is approximately half that of the end of the tip (0.59 and 1 mm, respectively) and to ease the handling of the device, the micropipette was placed vertically, with the head of the pin acting as WE contacting a conductive copper adhesive tape piece (3” Core, ½” (W) x 54 ft (L), Electron Microscopy Sciences) manually cut (5 x 25 mm) and located over the bench. Crocodile clamps were employed for connecting the copper tape (and then the WE) and the other two pins acting as electrodes to the potentiostat (Figure 1C). The device was clamped to a stand with a rod (as can be seen in Figure S1).

2.3. Electrochemical measurements

All measurements were done using a µAUTOLAB TYPE III (Metrohm) potentiostat. A volume of 360 µL of the working solution was aspirated into the tip to record cyclic (CV) or linear sweep (LSV) voltammograms, between +0.5 and -0.6 V. For both techniques, a scan rate of 0.1 V·s$^{-1}$ and a step potential of 0.002 V were used.

2.4. Determination of SDS (MB active substance) after extraction of the ion pair formed with MB

A modification of the standard method used for the determination of anionic surfactants as Methylene Blue Active Substances (MBAS) already described [24] was here employed. In this work, 1 mL of the sample (i.e. SDS solution in ultrapure water for optimizations or in tap water for real sample analysis) was mixed with 1 mL of a MB stock solution (25 µg·mL$^{-1}$ in 0.5 M HCl) and 1 mL of chloroform (CHCl$_3$). After shaking for 30 s, the phase separation took place. Usually is the absorbance of the organic phase containing the ion pair that is measured at 652 nm. But in this case, electrochemical measurements were performed in the aqueous phase located over the chloroform layer, by aspirating it into the tip and a LSV was recorded as commented in the previous section.

2.5. Determination of SDS without extraction.

In this case the procedure does not involve any extraction with chloroform. SDS influences the electrochemical signal of MB, and this was used to determine its concentration. Here, 360 µL of a solution containing SDS (in different concentrations) and a fixed concentration of MB (25 µg·mL$^{-1}$) were aspirated to record the LSV as commented in a previous section. The reduction current of MB changed according to the concentration of SDS in solution. This allowed to obtain a calibration plot for SDS concentration.

3. Results and discussion
The design of the electrochemical cell is based on the use of very cheap and available elements: pins and tips. Micropipette tips are also very versatile in regard to the size (volume) and materials. In this case we chose commercial polypropylene tips of 100-1000 µL volume, but a different polymer could be employed (even modified) and pins could be inserted in tips of lower/higher volume to adjust the volume of the electrochemical cell according to the requirements of the application. Pins are introduced unmodified in the upper part of the tip (RE and CE) but, depending on the volume, this height could be varied to ensure there is always ionic contact between the three electrodes. Even being very simple, the different parts of the pin can be used for different purposes. Hence: i) the sharp end allows to drill the polymeric tip material to insert horizontally the RE and CE. In this way, there is no need to make holes in the tip wall to introduce wires and, in turn, the addition of glue is not required. This simplifies the procedure and saves time since glue curing is not needed. Moreover, as a positive pressure has to be applied, the holes made are fully closed after insertion of the pins and the pressure required to aspirate solutions with the micropipette is maintained. ii) The stem is used directly as electrode (as for thread microfluidics [5]; in other previous works the electrode was the pinhead [6–8]), either modified with carbon ink (WE) or unmodified (RE and CE). In the last case, the part of the stem that is out of the tip can be used to connect the pins to the potentiostat using crocodile clips. iii) The head of the pin that is introduced vertically (WE) closes the tip at the bottom. With this design, the connection is easily made by contacting the pinhead with copper tape that is adhered on a flat substrate. The area of the WE could be changed by varying the length of the pin. In our case, we used 26-mm long stainless-steel pins. With a diameter of 0.59 mm, an approximated geometric area of 48.2 mm² was estimated (only the lateral area of the cylinder).

After the three electrodes were ready inside the micropipette tip, the new electrochemical platform was characterized. For this purpose, the electrochemical behavior of methylene blue (MB) was studied. To be oxidized, MB has to be first reduced to the leuco form [29]. In this redox process protons are involved, with oxidation favored at acid pH. Then, hydrochloric acid was chosen as electrolyte for the study. A volume of 360 µL of a 25 µg·mL⁻¹ MB solution in 0.5 M HCl was aspirated and a CV was recorded. As can be seen in Figure 2A, a reversible redox process can be observed with anodic and cathodic peak potentials at –0.02 and –0.08 V, respectively.
The intensity of the cathodic peak current was chosen as analytical signal. The precision between different pin-based WEs and different tip-based cells was studied recording LSVs in a 25 µg·mL\(^{-1}\) MB solution in 0.5 M HCl. When LSVs were performed using five different carbon ink pins-based WEs (washing with electrolyte between measurements) and maintaining the same micropipette tip and the same RE and CE, a relative standard deviation (RSD) of 5% for the cathodic peak current was obtained. The RSD obtained when the whole tip-based cell was changed (n = 5) was 7% for the cathodic peak current. These values demonstrated the adequate precision of the developed electrochemical device.

3.2. Effect of SDS in the redox process of MB

As a proof-of-concept, we proved the suitability of this new low-cost electrochemical cell to perform simple and sensitive determinations of molecules of interest. As it was reported in previous works, submicellar concentrations of surfactants (cationic or anionic) produced an increase in the intensity of the oxidation and reduction peak currents as well as in the reversibility of the electrochemical processes of aromatic species [30–33]. In those cases, the surfactant is introduced as a modifier of the carbon paste electrode (previously immersed in a surfactant solution [30,31,33]), or by further addition of the surfactant to the measurement solution [32] (approach followed in this work). Thus, the effect of SDS on the behavior of MB was studied recording LSVs with the micropipette tip-based cell in presence and absence of SDS (Figure 2B). The concentration of SDS (20 µg·mL\(^{-1}\), i.e. 7.0·10\(^{-5}\) M) was below the critical micellar concentration (2.4 mg·mL\(^{-1}\) in water [34]). MB was in slight excess compared to SDS (25 µg·mL\(^{-1}\), 7.8·10\(^{-5}\) M). As expected, a notorious increase in the cathodic peak current (from -17.84 to -29.83 µA) was observed when SDS was present in the measurement medium. Taking advantage of this, calibration curves performed by varying the concentration of MB between 0.5 and 30 µg·mL\(^{-1}\) in both cases (Figure 2C), showed a sensitivity two-fold higher when this concentration of SDS was present in the medium. Slopes of -1.71 (R\(^2\) = 0.996) and -0.84 µA (µg·mL\(^{-1}\))\(^{-1}\) (R\(^2\) = 0.996) were obtained with and without SDS respectively. In Figure 2C, it can also be observed that a wider linear range was achieved when SDS was added to the solution. This improvement is likely due to the formation of the ion pair between the MB and the surfactant, that is stabilized at the electrode surface (as in the case of SDS and catecholamines [30] or cationic surfactants with flufenamic acid [33] or nitrophenol [32]).

3.3. Determination of SDS using MB as indicator by both approaches: with and without extraction
High concentrations of surfactants could have important environmental consequences and their determination becomes relevant in water samples suspected of their presence. Based on previous results and taking advantage of the effect of SDS in the cathodic peak of MB (approach I in Figure 3A), a calibration curve for SDS was performed adding different SDS concentrations to a solution containing the same MB concentration (25 µg·mL⁻¹). As Figure 3B shows, the intensity of the cathodic peak current of MB (25 µg·mL⁻¹) increases with SDS concentration, following the equation
\[ I_{MB} (\mu A) = -0.26 \times C_{SDS} (\mu g\cdot mL^{-1}) - 9.56 \]
with a \( R^2 \) of 0.994. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as \( 3s_b/m \) and \( 10s_b/m \) respectively, where \( m \) is the slope of the calibration plot, and \( s_b \) is the standard deviation of the intercept. LOD and LOQ values thus obtained were 1.3 µg·mL⁻¹ (4.5·10⁻⁶ M) and 4.3 µg·mL⁻¹ (1.5·10⁻⁵ M) respectively.

A second approach for SDS determination (approach II in Figure 3A) was developed modifying the standard method to detect anionic surfactants [23]. This is based on the spectrophotometric measurement performed in the organic phase, which contains the ion pair SDS-MB. In this work we have only considered SDS since is the anionic surfactant usually present at higher concentration [22], but all the anionic surfactants that form ion pairs with MB (MBAS) could be determined jointly. After following the modified method explained in the experimental section, an aqueous and an organic phase were obtained after extraction with chloroform and phase separation. The organic phase contains the ionic pair MB-SDS and in the aqueous phase remains the excess of MB that has not reacted. In this case, the aqueous phase was aspirated inside the micropipette tip-cell for performing the electrochemical measurement. As the ion pair has been extracted, the analytical signal (intensity of the peak current of the cathodic process of MB) will be indirectly proportional to the concentration of anionic surfactants (SDS) in the sample.

For this study, different concentrations of SDS were tested using a fixed concentration of MB (25 µg·mL⁻¹). Each SDS solution (in ultrapure water) was mixed for 30 s with 1 mL of MB solution and 1 mL of chloroform as explained in the Section 2.4. After phase separation, the layer at the top was aspirated into the micropipette-tip-cell and the micropipette was clamped to the stand to proceed with the measurements.

As can be seen in Figure 3C, as SDS concentration increases, aqueous and organic phases (top and bottom) become lighter and darker respectively, due to the interaction of MB with SDS and further extraction with chloroform. In Figure 3D, a calibration graph with the measurements performed in the aqueous phase after phase separation for six different concentrations of SDS is shown, where \( I_{MB} \) is the intensity of...
the MB cathodic peak current obtained from a LSV recorded from +0.5 V to -0.6 V. As can be observed, the higher the SDS concentration, the lower the concentration of the remaining MB in aqueous phase and, in turn, the analytical signal. Thus, this intensity correlated linearly with the concentration of SDS following the equation \( I_{MB} (\mu A) = 0.37 C_{SDS} (\mu g \cdot mL^{-1}) - 13.78 \) with a \( R^2 \) of 0.997. A LOD of 1.2 \( \mu g \cdot mL^{-1} \) (4.2 \( \times 10^{-6} \) M) and a LOQ of 3.7 \( \mu g \cdot mL^{-1} \) (1.3 \( \times 10^{-5} \) M) were obtained using the above formula. Therefore, similar LODs were obtained for both methodologies, although the measurement after the extraction provides a slightly higher sensitivity (almost one and a half times).

### 3.4. Application to tap water samples analysis

In order to evaluate the accuracy of this new tip-based electrochemical device, both methods (with and without previous extraction) were probed with spiked water samples. Related to the possible interferences in real samples, two main cases could be considered. On the one hand, any compound that could be reduced at the potential of MB or lower could be considered as interferent. However, reduction processes in organic molecules are not as common as the oxidation ones, and the potential of reduction is not extremely negative. Moreover, instead of a chronoamperogram, a linear sweep or cyclic voltammogram is recorded, that could be more informative about the processes present. On the other hand, any anionic compound that could interact with cationic methylene blue could decrease its content in solution and behave as interferent when extraction is performed. This is the reason why the standard method on which we are based for SDS determination is reported as method for MBAS determination, in order to consider all the compounds. Similarly, when no extraction is carried out, other surfactants could increase the signal of MB. However, SDS is one of the main MBAS and the most common anionic surfactant. In case important interferences are suspected, a thorough study should be performed previously.

Tap water from a municipality (Lugones, Siero) located in the center of the Principality of Asturias, Spain, was spiked with two different SDS concentrations (8 and 17 \( \mu g \cdot mL^{-1} \)). Samples were analyzed by both methodologies and the results obtained are reported in Table 1. Using the equation of the calibration plot obtained with SDS standard solutions prepared in ultrapure water, recoveries between 93% and 111% for both concentration levels and both methods were obtained showing the feasibility of the tip-based cell and not important matrix effects of the method. The mean values obtained following both methodologies were statistically compared through a Student’s \( t \)-test: the \( t \) values calculated for the samples were lower than the tabulated \( t \) value for two degrees of freedom and a 0.05 significance level. Hence, we concluded that there
were no significant differences between the values for SDS concentrations determined following the two different procedures, demonstrating the accuracy of the methodology.

Table 1. Results of the recovery test in tap water samples for both methods for SDS determination (mean value ± standard deviation for three replicates).

<table>
<thead>
<tr>
<th></th>
<th>[SDS] added (µg·mL⁻¹)</th>
<th>[SDS] found (µg·mL⁻¹)</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>With extraction</td>
<td>8</td>
<td>7 ± 1</td>
</tr>
<tr>
<td></td>
<td>Without extraction</td>
<td>8</td>
<td>8 ± 1</td>
</tr>
<tr>
<td>Sample 2</td>
<td>With extraction</td>
<td>17</td>
<td>19 ± 1</td>
</tr>
<tr>
<td></td>
<td>Without extraction</td>
<td>17</td>
<td>17 ± 1</td>
</tr>
</tbody>
</table>

4. Conclusions

In-field analysis needs portable and simple devices and electroanalytical platforms have demonstrated to be very appropriate. In this context, a new electrochemical cell was fabricated in a very simple way using a micropipette tip and stainless-steel pins. Its good electroanalytical performance was demonstrated using methylene blue as known redox probe. Moreover, this novel tip-based cell was applied to real environmental analysis. It was applied to anionic surfactant determination, very relevant from the environmental point of view. SDS is a methylene blue active substance (MBAS) and can be determined indirectly measuring MB by voltammetry, which presents a reversible redox process at low potentials. Two approaches for SDS determination demonstrate the versatility of the tip-based cell to obtain accurate and precise results when both methods are compared.

The materials used are commonly found in most laboratories. Therefore, this do-it-yourself device becomes easily available worldwide. Tips and pins, that are mass produced, could be easily mass modified adding e.g., nanomaterials to the carbon ink of the working electrode, improving the final signal and obtaining better sensitivity. The availability of different types of micropipette tips and stainless-steel pins increases the possible applications of these versatile platforms.

Author Contributions

The manuscript was written through contributions of all authors.

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Figures captions

Figure 1. Schematic representation of the: A) different parts of the pin with their functions, B) modification of the stainless-steel pins used as working electrodes, C) electrochemical cell fabricated using a 100-1000 µL micropipette tip.

Figure 2. A) CV recorded in a 25 µg.mL⁻¹ of MB in 0.5 M HCl (scan rate 0.1 V.s⁻¹, step potential 0.002 V) using the micropipette tip-cell. B) Cathodic processes recorded by LSV in a 25 µg.mL⁻¹ MB solution without SDS and with 20 µg.mL⁻¹ of SDS (scan rate 0.1 V.s⁻¹, step potential 0.002 V) using the micropipette tip-cell. B) Calibration curve of MB without SDS and with 20 µg.mL⁻¹ of SDS. Error bars indicate the standard deviation of three replicates.

Figure 3. A) Scheme of both approaches (with and without extraction) for SDS determination using MB as indicator. B) Calibration graph employing the electrochemical measurements of MB obtained without extraction. C) Picture of microcentrifuge tubes with different SDS concentrations (0, 2.5, 5, 10, 20 and 30 µg. mL⁻¹) after phase separation using the modified standard method for the analysis of MBAS. D) Calibration graph employing the electrochemical measurements of MB obtained in the aqueous phase after performing the modified standard method for the analysis of MBAS. Each measurement was done in triplicate. Error bars correspond to the standard deviation of the measurements.
Figures

Figure 1

A

SHARP END
To drill the polymeric tip and insert counter (CE) and reference electrodes (RE)

STEM
To be used as modified or unmodified electrode

HEAD
To close the tip at the bottom and to connect with the copper tape

B

C

Counter electrode (CE)

Reference electrode (RE)

Working electrode (WE)

Conductive copper tape

Potentiostat

$x \leq 70^\circ C$

Carbon ink
Figure 2
Figure 3

**A** Approach I: without extraction
- i) Background signal
- ii) SDS Signal

**Approach II: with extraction**
- Step 1
- Step 2

Excess of MB in aqueous phase (a higher concentration of SDS in the sample decreases the concentration of MB in aqueous phase).

**Figure B**

**Figure C**

**Figure D**
- Simple pin-based design for an electrochemical cell employing a micropipette-tip
- Low-cost electroanalysis using stainless-steel pins and micropipette tips
- Fast analysis of surfactants using micropipette-tip based electrochemical cells
- Electrochemical determination of SDS using a low-cost approach using pins and tips.
- Water analysis for electrochemical determination of surfactants
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.