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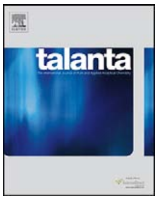

Highly sensitive CNT composite amperometric sensors integrated in an automated flow system for the determination of free chlorine in waters

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ABSTRACT

We report the benefit of using an optimized composite electrode, based on a multiwall carbon nanotubes and epoxy resin, as working electrode in an automated flow system. The optimal composite electrode composition consists in a 10% carbon nanotubes and 90% epoxy resin. This composition provides lower limit of detection and increases the stability and reproducibility of the analytical signal compared to the 20% conventional composition electrodes. Moreover, the standard solutions are on-line prepared with an automated flow system. The integration of the developed carbon nanotube electrodes in the proposed flow system provides a highly sensitive analyzer for free chlorine determination in water down to the 20 μg L^{-1}. The working range was found to be 0.02–4 mg L^{-1} with an analysis time of 60 s. The system sensitivity was maintained into the control limits ($\pm 2\sigma$) for one month, with a mean value of -0.146 (± 0.008) μA L mg^{-1}. Validation of the analytical system has been performed by the successful determination of free chlorine in tap water and swimming pools water samples.

1. Introduction

Conducting composite materials have been of great interest for many years because of their versatile use in the electrochemistry field, particularly in sensor devices. It is known that the electrochemical properties of carbon composite electrodes present some improvements over conventional solid carbon electrodes (glassy carbon, graphite, etc.), such as easy surface renewal, low background current and efficient mass transport, among others. Moreover, their high malleability, before being hardened, permits an easy incorporation of a variety of reagents, enzymes and chemical recognition agents [1,2].

Currently, high interest is focused on composites based on carbon nanotubes (CNTs), because of their remarkable mechanical and electrical properties [3,4] and other advantages when compared to other carbon allotropic forms, such as a higher area to volume ratio, lower resistivity and high mechanical and chemical stability. Several configurations of CNT electrodes have been reported previously, such as those randomly adsorbed on glassy carbon electrodes [5,6] or dispersed in an inert matrix [7–10]. This last configuration provides attractive electrochemical properties since the polymeric matrix, together with the CNTs, confer mechanical robustness and high electric conductivity to the final composite electrode.

An important feature of composite electrodes is that their final analytical performance is strongly influenced by the carbon load within the polymeric matrix [11]. Some parameters, such as the composite resistivity, the background capacitance current, the material stability and the heterogeneous electron transfer rate, depend on this factor. It is well known that, regarding to the background capacitance current, the electrode capacitance value is directly related to the amount of exposed carbon. Besides, depending on the carbon load, composite electrodes can behave similar to a microelectrodes array. This way, a more efficient mass transfer of the electroactive species due to radial diffusion on the spaced carbon particles is obtained. Consequently, a careful characterization and optimization of the carbon loads in the composite material results mandatory [12,13].

Up to now, the optimization of the composite proportion has been done under the criterion of maximizing the carbon load until lose of physical and mechanical stability appears. The aim of this approach is to achieve the minimum composite resistivity value [7,14,15]. Nevertheless, using this criterion, other important parameters, such as background capacitance current and heterogeneous electron transfer rate are not considered. In order to correct those effects, an exhaustive study regarding the characterization and optimization of the CNT loading in a polymeric matrix (epoxy resin, Epotech H77) to improve its electrochemical properties was previously performed [12]. In that previous work, each parameter was evaluated varying the carbon load in the composite. The optimal composite (10%, w/w, CNT loads) combined easy manipulation during the fabrication procedure, low background current and an

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improved response compared to the conventional conducting composite electrodes used in the vast majority of works reported using a higher carbon load (20%, w/w, CNT loads) [7,14,16]. In this study free chlorine determination in waters was performed following this approach in order to demonstrate the advantages of the optimized composite when compared to conventional composite electrodes [7,14]. The optimal amperometric composite electrode was integrated in a continuous flow injection analysis (FIA) system to take advantage of all the benefits provided by this technique. The composite material was easily integrated in the flow system due to its high malleability before hardening, which provides high versatility to produce electrodes in any desires shape to match any experimental set-up. The analytical response of 10% and 20% composite electrodes was evaluated and compared. The benefits of using 10% composite electrodes in terms of analytical performance and device stability are described. In this sense, the successful analysis of chlorine in complex matrix provided from a public swimming pool and a tap water supply were carried out at extremely low concentrations with excellent quantification results.

2. Experimental

2.1. Devices and apparatus

Voltammetric measurements were performed using a computer controlled AUTOLAB PGSTAT12 potentiostat/galvanostat (EcoChemie, Utrech, The Netherlands). Electroanalytical experiments were carried out in a 10 mL glass cell (homemade), at room temperature (25 °C), using a three-electrode configuration. A platinum-based electrode 52-671 (Crison Instruments, Alella, Barcelona, Spain), a Ag/AgCl single junction ORION 900100 (Thermo Electron Corporation, Beverly, MA, USA) and the constructed CNT composite electrodes were used as counter, reference, and working electrodes, respectively.

Amperometric measurements, for the FIA system, were performed using an amperimeter LC-4C (Bioanalytical 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 recording and visualization. A CNTs composite working electrode was inserted in a homemade flow cell (50 mm^3 internal volume) based on two methacrylate blocks described elsewhere [17]. A single junction Ag/AgCl reference electrode ORION 900100 was placed downstream the flow cell by means of a methacrylate assembly. Fig. 1A shows the conventional-FIA system configuration that was used in previous works [18]. Fig. 1B shows the improvement of the experimental manifold used in this work. The manifold of the improved-FIA system includes a three-way solenoid valve, NResearch 161T031 (NResearch Incorporated, West Caldwell, NJ, USA) controlled by a virtual instrument especially developed for this application [19]. A four-channel peristaltic pump (Gilson Company, Inc., Columbus, OH, USA) for liquid pumping equipped with 1.14 mm internal diameter silicon tubing (Elkay Products) and 0.7 mm internal diameter Teflon tubing (Omnifit) were used to connect the system components.

2.2. Chemicals and reagents

All solutions were prepared using Milli-Q deionized water (Millipore, Billerica, MA, USA). Sodium hypochlorite (10–13%), potassium dihydrogen phosphate (99.5%) and potassium chloride (99.5%), A.C.S grade, were obtained from Sigma–Aldrich (St. Louis, MO, USA) and used without further purification. L-purified multiwall carbon nanotubes growth 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, supplied by Epoxy Technology (Epoxy Technology, Billerica, MA, USA), were used as polymeric matrix.

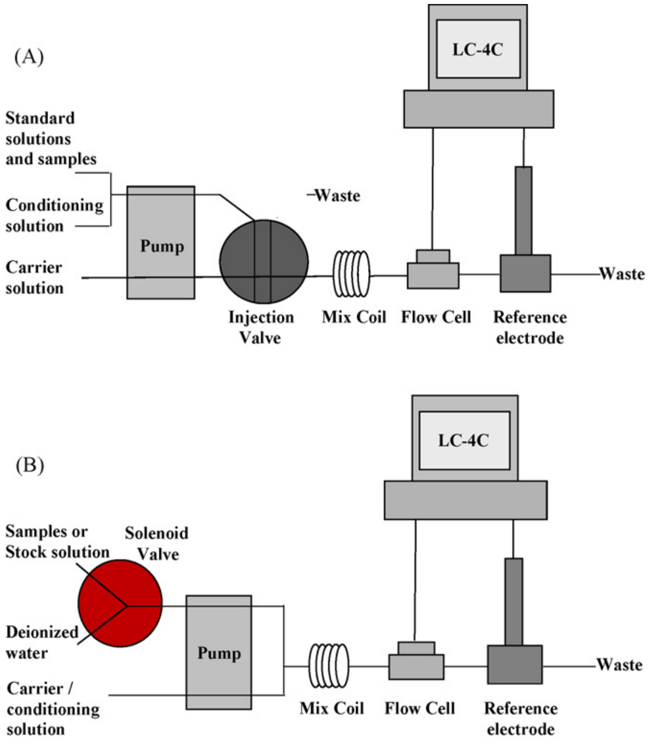

Fig. 1. Experimental manifold used for chlorine determination in (A) a conventional-FIA system and (B) an improved-FIA system.

2.3. Fabrication of the carbon nanotubes composite electrodes

Working electrodes used in voltammetric measurements were prepared following the conventional methodology described in a previous work [20]. The composite based working electrode was prepared by mixing polymer EpoTek H77A and its corresponding hardener (EpoTeK H77B) in a 20:3 (w/w) ratio and adding a 10% and a 20% (w/w) load of multiwall carbon nanotubes (MWCNTs). The composite mixtures were homogenized for 60 min and were allowed to harden during 24 h at 80 °C [7,14]. Electrode surfaces were later polished with different sandpapers of decreasing grain size. The resultant geometric area for the final working electrode was 28 mm^2. However, its integration to the flow cell [17] resulted in a geometric area of 10 mm^2.

2.4. Analytical performance

All experiments were performed at room temperature. Voltammetric measurements were performed to define the optimal amperometric detection potential. These experiments were carried out, under quiescent conditions, in a 0.1 M phosphate buffer solution (PBS) at pH 5.5, containing 0.1 M potassium chloride as conducting electrolyte. Chlorine detection in the FIA system was carried out applying a potential of −100 mV (vs. Ag/AgCl). Chlorine analytical response was evaluated, in the concentration range of 0–4 mg L^{-1}, prepared by dilution of the stock solution in deionized water. The preparation of standard solutions in the FIA systems was performed as follows: for the conventional-FIA system (Fig. 1A), standards were prepared off-line by dilution of the stock solution (2000 mg L^{-1}) in deionized water. The standard solutions/samples were then pre-treated by its dilution (1:1) in a 0.2 M PBS and 0.2 M KCl at pH 5.5 pre-treatment solution [17]. This pre-treatment step allows adjusting ionic force and pH of the standard solution/sample, before being analyzed. A 0.1 M PBS and 0.1 M KCl at pH 5.5 solution was used as carrier. On the other hand, for the improved-FIA system (Fig. 1B), the standard solutions were online prepared from one stock solution (5 mg L^{-1}) by means of an automatic multicommutation [21–23] technique. In general, this technique is applied in continued flow systems by means of the use of discrete commutation devices (three-way solenoid valve). The definition of different frequencies of valve commutation (on/off), combined with a constant flow rate, allow us to create sequences of standard stock/deionized water (binary sampling) of *n* aliquots which interpenetrate themselves, producing the dilution need for each different standard concentration. The injection volume is controlled by measuring the time that the standard stock/deionized water or sample flows through the system. In fact, here the different standard solutions were prepared by means of different duty cycle applied to the digital signal that controls the commutation system. The overall commutation binary time was 18 s and the mixing ratios to obtain the desired concentrations were 0.8/0.2, 0.6/0.4, 0.4/0.6, 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.

A 0.2 M PBS and 0.2 M KCl at pH 5.5 solution was used as carrier/conditioning solution. The standard solutions/samples were also diluted (1:1) by the carrier/conditioning solution, before being analyzed.

Sixteen swimming pool water samples were used as real samples, fourteen doped samples were prepared by dilution of the stock solution in real samples and two synthetic samples, used as control, were prepared by dilution of the stock solution in deionized water. In addition, four more samples were collected from the tap water supply system. To validate the method and to avoid samples decomposition, due to chlorine instability, samples were immediately analyzed using simultaneously the improved-FIA system and the standard DPD colorimetric method [24–26]. The DPD method consisted in a commercial colorimeter (HACH, Düsseldorf, Germany) that provides direct measurements in mg L^{-1} units.

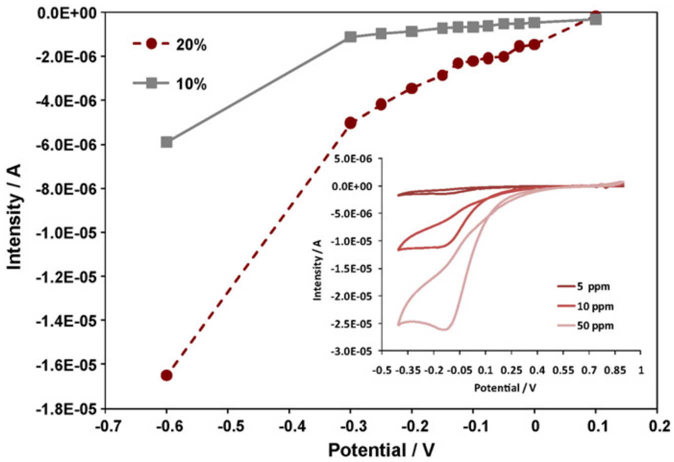

Fig. 2. Free chlorine hydrodynamic curve recorded with both 10% and 20% composite electrodes. The used free chlorine concentration was 2 mg L^{-1}. The inset shows voltammogram plots for different amounts of free chlorine in PBS at pH 5.5. Scan rate: 100 mV s^{-1}.

3. Results and discussion

3.1. Characterization of the flow system

Fig. 2 shows the hydrodynamic curve and cyclic voltammetric plots of the experiments carried out in order to determine the appropriated polarization potential. The voltammogram plots are depicted in Fig. 2. It can be observed that at a potential around −100 mV (inset Fig. 2), the free chlorine reduction over the CNT composite electrode took place without the interference of the dissolved oxygen. The hydrodynamic curve showed a plateau at which the reduction of the free chlorine took place. This plateau expanded

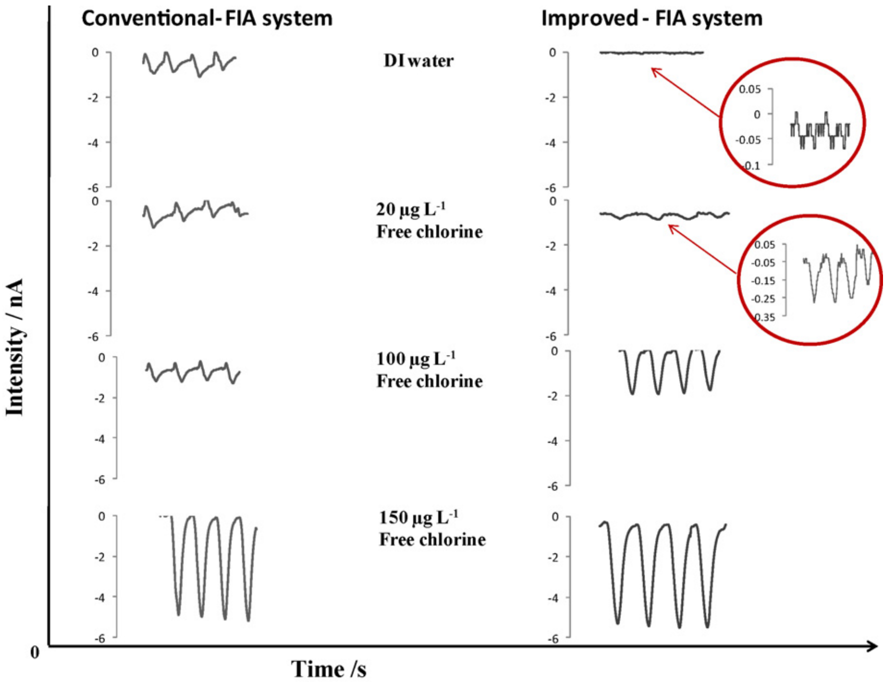

Fig. 3. Different analytical signals recorded for different low concentration of free chlorine and water (blank solution), using the 10% composite electrode, for both conventional-FIA and improved-FIA system.

from −50 to −125 mV and from −75 to −200 mV for both, 20% and 10% CNT, composite electrodes, respectively. Therefore, a potential of −100 mV was chosen for subsequent measurements.

In order to find the optimal hydrodynamic experimental parameter, face centered cube experimental design was used. The design included seventeen experiments. The injection volume was evaluated in a range between 300 and 800 μL, the flow rate between 1 and 2.8 mL min^{-1} and the mix coil length between 50 and 147 cm. After evaluation, these parameters were considered optimal at 600 μL, 2 mL min^{-1}, and 53 cm, respectively. These experimental conditions improved the system sensitivity, maximized its analytical response and minimized reagents consumption. The analysis time for sample was found to be 1 min (time from injection to steady-state signal).

The main enhancement that provides the improved-FIA system was noticed when analyses at low concentrations were performed. Fig. 3 shows the amperometric recording for different injections of low concentration of free chlorine and blank solution (deionized water), for both, conventional-FIA and improved-FIA systems, using the optimized 10% composite electrode. Using the conventional-FIA system, it was not possible to detect concentrations under 150 μg L^{-1}. The small variations observed in the baseline for lower concentrations could be associated to the injection-valve commutation, which generates a transitory signal every time the sample is injected. This valve-effect masks the signal of the sensor, and avoids the system to respond to low concentrations. This drawback was overcome by replacing the injection-valve by a three-way solenoid valve. The new system was capable of analyzing free chlorine concentration of even 20 μg μL^{-1} after manifold improvements were performed.

3.2. *Amperometric flow injection analysis*

The CNT composite electrodes response to different free chlorine concentrations was evaluated with the amperometric technique, using the improved-FIA system. Different analytical parameters such as baseline stability, repeatability of the signal, reproducibility and linear response of the system for both electrode compositions, 20% and 10% of CNT, were evaluated.

It is well known that the analytical signal in FIA is determined by the difference between the maximum and the baseline. Consequently, a stable baseline is needed to make an accurate determination. To evaluate the baseline stability for both, 20% and 10% CNT composite electrodes, the background current was registered during 2 h using the optimal experimental conditions. A stable baseline, with a drift of about 0.01 nA min^{-1}, was observed for the 10% composite electrode. On the other hand, the 20% composite electrode presented a baseline more unstable, with a drift of about 1 nA min^{-1}, 100 times higher than that obtain with 10% composite electrodes and with higher background noise.

In order to evaluated the repeatability of the signal for both compositions, a 2 mg L^{-1} free chlorine standard solution was used. For the 10% composite electrode, a RSD of 2% was obtained for 30 replicates performed consecutively (95% confidence). The mean peak current value was found to be −0.300 (±0.002) μA. On the other hand, the 20% composite electrode presented a RSD of 3% for 30 replicates (95% of confidence). The mean peak current value obtained in this case was slightly higher, −0.38 (±0.01) μA, as expected.

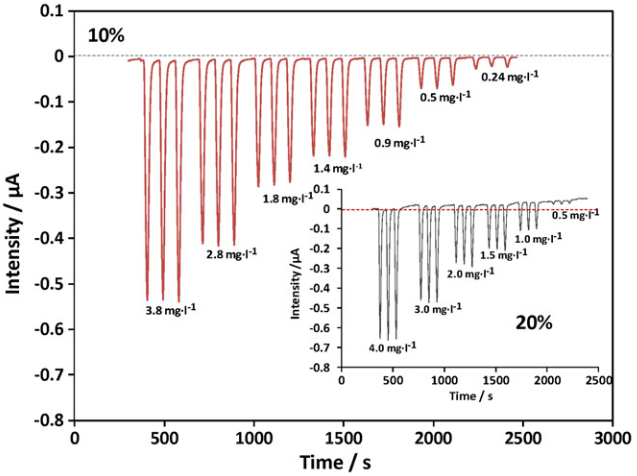

Fig. 4. Records of the amperometric signal with the improved-FIA system for both 10% and 20% (inset figure) composite electrodes.

The response of both electrodes was evaluated, using the improved-FIA system, in a range between 0 and 4 mg L^{-1}. Fig. 4 shows the analytical response in this range. This concentration range was chosen because it matches the minimum and maximum legal chlorine concentration permitted by the current Spanish legislation in swimming pool water [27] and tap water [28]. Table 1 shows the calibration parameters for 10% and 20% composite electrodes. It is important to highlight that even with a lower carbon load in the 10% composite electrodes it is possible to achieve a sensitivity similar to that obtained with 20% composite electrodes. The limit of detection (LOD) was estimated by the $S/N = 3$, $n = 50$ criterion [29]. Under this condition, the LOD for the 10% composite electrode is 8.5 times lower than that obtained for 20% ones. Even though the LOD for both composite electrodes were suitable to perform chlorine analysis in both swimming pool and tap water samples, notorious improvements in the analytical response, in terms of signal stability, system reproducibility and LOD, were observed for the 10% composite electrodes compared to the 20% ones. Moreover, the LOD value achieved with the 10% composite electrode is lower or comparable regarding previous works using more expensive amperometric transducer materials, such as gold [18,30,31] or platinum [32].

Taking into account these improvements, 10% composite electrodes were selected and subjected to further studies. An estimation of the sensor lifetime was carried out, for 10% composite electrodes, by means of different calibration experiments performed during 30 consecutive days. The mean value of the calibration plots carried out on the first working day (−0.146 (±0.008) μA L mg^{-1}, $n = 3$, 95% of confidence) was used to calculate the control/nominal sensitive value. The upper and lower control limits were set as 2 times the standard deviation (2σ) of this value. The results showed that after one month of use the sensitivity was still within the control limits.

Table 1
Calibration parameters for 10 and 20% composite electrodes.

Electrode	Intercept[a]	[a]Slope (μA L mg^{-1})	r^2	[a]$\text{RSD}_{\text{slope}}$ (%)	LOD (μg L^{-1})	[b]Analysis time (s)
10%	0.02(±0.01)	−0.15 (±0.01)	0.995	3	20	60
20%	0.01(±0.01)	−0.19 (±0.02)	0.997	5	170	58

[a] $n = 3$, 95% confidence level.
[b] Time from injection to steady-state signal.

Table 2
Free chlorine analysis in swimming pool water samples with the DPD colorimetric standard method as well as the improved-FIA system and the recovery value.

Sample	[a]DPD colorimetric standard method (mg L^{-1})	[b]Improved-FIA system (mg L^{-1})	Recovery (%)
Swimming pool water sample			
1	0.86	0.78 (±0.09)	91
2	0.53	0.47 (±0.03)	89
3	3.2	3.32 (±0.07)	104
4	0.46	0.49 (±0.5)	106
5	1.51	1.55 (±0.03)	103
6	0.89	0.85 (±0.06)	95
7	1.35	1.3 (±0.1)	96
8	0.65	0.61 (±0.02)	94
9	1.17	1.17 (±0.04)	100
10	2.1	1.9 (±0.2)	91
11	1.14	1.03 (±0.06)	90
12	1.15	1.2 (±0.1)	104
13	1.14	1.2 (±0.3)	105
14	0.52	0.48 (±0.03)	92
15	0.98	1.00 (±0.08)	102
16	1.08	1.09 (±0.06)	101
Doped sample			
17	1.60	1.58 (±0.01)	99
18	1.85	1.8 (±0.1)	97
19	1.45	1.35 (±0.04)	93
20	1.21	1.18 (±0.07)	98
21	1.77	1.8 (±0.1)	102
22	1.39	1.46 (±0.07)	105
23	3.2	3.1 (±0.1)	97
24	1.46	1.45 (±0.03)	99
25	1.94	1.87 (±0.03)	96
26	1.45	1.5 (±0.1)	103
27	1.88	2.03 (±0.01)	108
28	2.8	2.56 (±0.06)	91
29	0.84	0.75 (±0.07)	90
30	4.3	4.2 (±0.2)	98
Tap water samples			
31	0.42	0.39 (±0.01)	93
32	0.35	0.34 (±0.01)	97
33	0.41	0.38 (±0.05)	93
34	0.35	0.35 (±0.01)	100
Synthetic samples			
35	1.60	1.71 (±0.03)	107
36	1.04	0.99 (±0.01)	95

[a] The typical precision of the standard method for samples with free chlorine concentration <2 mg L^{-1} is ±0.05 and for concentration >2 mg L^{-1} is ±0.2, at 95% confidence level.

[b] $n = 3$, 95% confidence level.

3.3. *Validation of the analytical system using real samples*

To validate the system performance, thirty-six samples were analyzed during several days. Sixteen of them were directly collected from the swimming pool, and fourteen were doped after collected with the chlorine stock solution. Two samples were synthetically prepared and used as control. In addition, four more samples were collected from the tap water supply system. Table 2 shows the obtained results in the sample analysis using both methods and the recovery value. Statistical paired *t*-test and the least-square linear regression were used throughout. No significant differences were observed at 95% confidence level. In paired *t*-test: $t_{\mathrm{cal}} = 1.533 < t_{\mathrm{tab}} = 2.030$, while in the least-square linear regression a slope of 0.99 ± 0.01 and an intercept of 0.01 ± 0.02 were obtained. The correlation coefficient was $r^2 = 0.990$.

4. Conclusions

Composite electrodes based on CNT (10 and 20% loads) and epoxy resin have been integrated in a FIA system and tested for the continuous analysis of free chlorine standard solution at very low concentrations. As demonstrated in this work, the use of a 10% optimized composite presented significant electrochemical advantages respect to the 20% equivalent. The 10% composite electrodes showed better LOD as well as an increase of the stability and repeatability of the analytical signal.

Moreover, the FIA system improved by means of the multicommutation approach for on-line standards preparation provided an enhancement of the analytical signal. The improved flow manifold rendered more stability and robustness to the system, allowing the determination of previously undetectable free chlorine concentrations when using the conventional flow system. Furthermore, it also allowed to reduce reagents consumption and the determination of lower free chlorine concentration down to 20 μg L^{-1}.

Finally, an excellent agreement between the obtained results with the proposed system and the standard method for free chlorine determination was obtained, demonstrating the high potential of the optimized composite electrode integrated in the improved-FIA system. Moreover, the developed system provides sensitive, robustness and automation, which makes it suitable for on-line monitoring low concentrations of others electroactive species.

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