



# Disposable sensor for electrochemical determination of chloride ions



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## ABSTRACT

This work describes the development of a new, simple and inexpensive method for the determination of chloride ions, by using voltammetric disposable sensors. The sensor includes three screen printed electrodes: a working, an auxiliary (both carbon based paste electrodes), and a pseudo-reference Ag/AgCl paste based electrode. Since the presence of chloride ions in the solution modifies the equilibrium potential of Ag/AgCl electrode, the concentration of this analyte has been determined through the systematic shift of the voltammetric peak potential of a control species such as potassium ferricyanide, potassium ferrocyanide or ferrocenemethanol. These control species can be used in solution or mixed into the carbon paste of the working screen printed electrode.

In order to characterize the developed methods, reproducibility, repeatability and detection limit of the sensors were calculated in each case. Reproducibility values below 3% ( $n=5$ ) were obtained. When ferrocenemethanol was used as control species, the lowest quantity of chloride ions detected was 10.0 mM. A comprehensive study of interfering ions was also carried out.

These sensors were successfully applied to determine the chloride content in sea water and in a commercial saline solution sample.

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## 1. Introduction

Since the 1990s, screen-printing technology, adapted from the microelectronics industry, has been profusely used to develop electrochemical sensors, biosensors and immunosensors. Screen-printed technology consists of layer-by layer deposition of ink upon a solid substrate, through the use of a screen or mesh, defining the geometry of the sensor [1].

Screen-printed electrodes (SPEs) avoid some of the common problems of classical solid electrodes, such as memory effects and tedious cleaning processes, and offer many advantages such as simplicity, low cost, reproducibility, versatility etc. [2,3].

Moreover, these devices hold great promise for on-site monitoring and are made in serial production, so the electrochemical determination of a wide range of substances is currently undergoing widespread growth in many fields such as food, biomedical or environmental [4,5]. The adaptability of SPEs is also of great benefit in areas of research; the ability to modify the electrodes with ease, through different inks commercially available for the reference, counter, and working electrodes, allows for highly specific and finely calibrated electrodes to be produced for specific target analytes [6].

The standard screen-printed electrochemical systems used in the construction of sensors include a working, a reference and an auxiliary electrode. For their construction successive layers of different inks were printed onto a PVC strip substrate using several screens [6]. While lots of different conductive pastes had been used to manufacture working or auxiliary electrodes, pastes based of Ag or Ag/AgCl are usually used to develop pseudo-reference electrodes (PRE) [7,8].

Although scientific interest is primarily devoted to working electrodes, progress with regard to the reference electrodes can also be ascertained, especially for measurements at which it is also important to maintain a reasonably constant comparative potential value for a defined measuring period [9,10].

In conventional reference electrodes, the Ag/AgCl wire is usually isolated from the solution by a nanoporous ceramic or glass frit and kept in a KCl solution of defined concentration. Owing to the frit, large molecules or ions cannot pass through this barrier, which establishes an ohmic contact between the reference electrode and the sample solution, restricting chemical exchange. However, quite often, PREs are used for on-chip sensors and biosensors due to convenience and the need for miniaturization. Unlike reference electrodes, these electrodes are not isolated from the sample solution, and, therefore, present certain disadvantages regarding potential stability. Nevertheless, the electrochemical properties of the electrode material and its chemical reactivity may play a significant role in the shape of acquired voltage signals [11,12].

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When working with screen-printed electrode systems, it must be taken into account that the potential of PREs is also affected by the medium composition becoming the most important handicap of this kind of device in some applications.

Alternatively, the variation of the equilibrium potential of the PRE by the presence of species, such as chloride ions, which form stable compounds with the components of PRE, can be used as an indicator of the presence of these species, and even allow their quantification.

Chloride ion sensing is important in many fields such as clinical diagnosis [13,14], environmental monitoring [15–17] and industrial applications [18,19]. Particularly the content of chloride ions in waters has been well monitored [20–22]. Seawater is essentially a fairly concentrated solution of various salts. The salt content, i.e. the amount of inorganic substance in solution, is designated as salinity and expressed in g/kg seawater or parts per thousands (‰), with sodium, magnesium, calcium and potassium as predominant cations, and chloride, sulfate, bromide and hydrogen carbonate as predominant anions. Since the chemical composition of seawater remains essentially constant, the measurement of only one chemical constituent is enough to determine the salt content. Therefore, salinity is normally determined by measuring the chloride content because chloride is the most abundant anion in sea water [23].

Numerous analytical methods for chloride ions determination including ion chromatography [24], near-infrared spectrometry [25], spectroscopy [26], light scattering [27], turbidimetric [28] and flow based methods coupled with different detectors [24,29,30] have been developed. Regarding electrochemical techniques, amperometric and potentiometric methods have been also described [31,32]. Potentiometric methods based on ion selective electrodes have been most frequently used, and several sensors for selective chloride ion detection have been suggested [14,19,24,29,33–37].

In the literature, despite the advantages of using SPEs, electrochemical determination of chloride ions using this kind of sensors was hardly found [38,39]. Most of them involve silver nanoparticles based SPEs [40–42].

This paper describes the development of a novel, inexpensive, highly simple, and disposable sensor for the determination of chloride ions. It is based on the systematic shift of the voltammetric peak of a control species when chloride ions are present in solution. In order to study its influence, different control species were tested. Since potassium ferricyanide ( $K_3[Fe(CN)_6]$ ), potassium ferrocyanide ( $K_4[Fe(CN)_6]$ ), and ferrocenemethanol (FeMeOH), show low redox potentials, they were chosen as control species in this study.

Control species were used in two different ways: In the first one, these were added in the sample solution, and in the other way, the control species were mixed into the carbon paste used to build the working screen-printed electrode.

The disposable character and simplicity of the device provides an interesting alternative to the most frequently used potentiometric method.

## 2. Material and methods

### 2.1. Reagents and solutions

All the reagents used were of analytical grade and Milli Q water (Millipore, Bedford, USA) was employed for preparing all solutions.

KCl, KBr,  $KNO_3$ ,  $K_2SO_4$ ,  $K_3[Fe(CN)_6]$  and  $K_4[Fe(CN)_6]$  were purchased from Merck (Darmstadt, Germany). Ferrocenemethanol was obtained from Sigma-Aldrich (Steinheim, Germany). KCN,  $Hg_2Cl_2$  and  $PbCl_2$  were provided by Panreac (Barcelona, Spain).

$Na_2CO_3$ ,  $K_2CrO_4$  and  $K_2Cr_2O_7$  were obtained from Fluka Chemika (Buchs, Switzerland).  $KBrO_3$  was purchased from Productos Químicos Kurz, (Barcelona, Spain).

C10903P14 (carbon ink), C2070508P4 (carbon with ferrocyanide ink) and D2071120D1 (dielectric ink) were purchased from Gwent Electronic Materials (Torfaen, U. K). Electrodag 6037 SS (Ag/AgCl ink) and Electrodag 418 (Ag ink) were supplied by Acheson Colloiden (Scheemda, The Netherlands).

Sea water was collected from Cantabrian Sea, Spain. The commercial saline solution (Vitulia) was obtained from a local pharmacy.

### 2.2. Apparatus

Voltammetric measurements were performed with a  $\mu$ Stat 200 bipotentiostat from Dropsens (Oviedo, Spain), using the DropView software package to control the instrument, register and perform the analysis of results.

Potentiometric measurements were made using chloride-selective electrode pH & ION-Meter GLP 22+Crison (Crison Instruments, Barcelona).

### 2.3. Sensor manufacturing

SPEs were home-produced on a DEK 248 printing machine (DEK, Weymouth, UK) using polyester screen, according to the procedure described elsewhere [1,43]. Silver and carbon inks were used in manufacture of SPEs. Electrode system consists of a carbon working electrode (area,  $12.56 \text{ mm}^2$ ), a carbon counter electrode and a Ag/AgCl PRE.

Carbon working SPEs modified with  $K_4[Fe(CN)_6]$  ( $SPC_{K_4[Fe(CN)_6]}Es$ ) were prepared by using C2070508P4 commercial ink. Carbon working SPEs modified with  $K_3[Fe(CN)_6]$  ( $SPC_{K_3[Fe(CN)_6]}Es$ ) or FeMeOH, ( $SPC_{FeMeOH}Es$ ) were prepared by incorporating a 3% (w/w) proportion of each compound directly into the C10903P14 carbon ink for printing the working electrodes.

### 2.4. Electrochemical measurements

When using carbon working SPEs, voltammetric measurements were accomplished in a single drop (200  $\mu$ L), containing  $5 \times 10^{-4} \text{ M } K_3[Fe(CN)_6]$ ,  $5 \times 10^{-4} \text{ M } K_4[Fe(CN)_6]$  or  $2 \times 10^{-4} \text{ M } FeMeOH$  and the chloride ions sample was deposited onto the surface of the electrochemical system. In the cases of using  $SPC_{FeMeOH}Es$ ,  $SPC_{K_3[Fe(CN)_6]}Es$  or  $SPC_{K_4[Fe(CN)_6]}Es$  a drop of sample solution, containing chloride ions, is directly deposited onto the surface.

Cyclic and differential pulse voltammograms were recorded between  $-0.4 \text{ V}$  and  $+0.8 \text{ V}$  when using FeMeOH or  $K_4[Fe(CN)_6]$  and, between  $+0.8$  and  $-0.4 \text{ V}$  in the case of using  $K_3[Fe(CN)_6]$ . All the measurements were taken at a scan rate of  $20 \text{ mV s}^{-1}$  and 10 mV of step potential.

## 3. Results and discussion

When using the screen-printed PREs, as already described above, the equilibrium potential of these electrodes can be altered by the presence in the sample of some species which can interact with silver or chloride ions. In fact, it was observed that the voltammetric peak of a reference species moves when ions such as carbonates, chlorides, bromides, etc. are added to the sample, due to the change in the equilibrium potential of PREs.

In this way, the presence of chloride ion produces a systematic shift of the peak potential of a reference electrochemically rapid system (control system). This shift is related to the amount of chloride in the medium, and it allows the determination of

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