



Electrochemical detection of free chlorine at inkjet printed silver electrodes



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ABSTRACT

A low-cost, reliable and sensitive electrochemical method for free chlorine analysis in water using inkjet printed silver electrodes is presented. Free chlorine detection was based on linear sweep voltammetry (LSV) analysis of AgCl/Ag₂O films formed over an inkjet printed silver electrode by the spontaneous reaction between silver and free chlorine species (*i.e.* HClO and ClO⁻) present in solution. The formation of AgCl/Ag₂O films was studied and characterized by high resolution scanning electron microscopy (HR SEM) and X-ray photoelectron spectroscopy (XPS) techniques. LSV characterization demonstrated a quantitative linear relationship between the amount of AgCl/Ag₂O formed and the concentration of free chlorine in water within a range from 1 to 100 ppm. After optimization of several parameters (*e.g.* scan rate, reaction time, starting potential), lowest detectable free chlorine concentration was 0.4 ppm (by standard addition method), while the limit of detection (*S/N* = 3) was equal to 2 ppm, with a sensitivity of 30 μC/ppm. The validation of the proposed methodology was performed by comparison with the standard *N,N*-diethylparaphenylenediamine (DPD) method for analyzing swimming pool water samples. Finally, it was demonstrated that reproducible and disposable silver electrodes could be easily prepared by inkjet printing in a large scale and in any required geometry to fit on-line and on-site free chlorine analyses requirements.

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1. Introduction

Free chlorine is a strong oxidizing agent widely used in the treatment of drinking water, swimming pools, waste waters, as well as in paper, food and rubber industries [1,2]. In water treatment, chlorine is usually added either in its gaseous form (Cl₂), or as the sodium or calcium hypochlorite salt, since Cl₂-containing aqueous solutions lead to the formation of hypochlorous acid through the reaction [3]:



However, depending on pH, hypochlorite (ClO⁻), rather than HClO (or a mixture of both) can be formed, the p*K*_a of the corresponding acid–base reaction being 7.4. Therefore by definition, the sum of the amounts of HClO and ClO⁻ present in an aqueous system is called free chlorine. This does not account for the chlorine added, but only to the chlorinated species that still remain after reaction with any oxidizable species (*i.e.* organic or metal species) present in the sample. Commonly, the presence of free chlorine in water is related to the absence of

disease-causing organisms and therefore is an indicator of microbiological safety [3–5]. However, an excess of free chlorine may result in irritation and difficulties for breathing, while in abnormal quantities it can cause serious damages to biological systems and lead to atherosclerosis, arthritis and cancer [6–9]. Drinking water has a very low free chlorine concentration limit (*i.e.* 0.2 ppm), while that of swimming pools is higher (*i.e.* 2 to 5 ppm) [9]. Total residual chlorine in water discharge from water treatment plants is usually in the range 0.6 to 1 ppm [10, 11]. According to the U.S. Department of Agriculture (USDA), the level of free chlorine in poultry chiller makeup water and in reuse waters should not exceed 50 and 5 ppm, respectively [5]. Therefore, measuring free chlorine content in water is of high relevance for many applications, and the implementation of fast, cheap and sensitive new methodologies for environmental monitoring is well justified.

Common analytical methods, such as colorimetric, spectrophotometric [2,12], chemiluminescence [13], chromatography coupled to mass spectrometry (*i.e.* electrophilic addition to styrene) [1], as well as iodometric and amperometric titrations have been employed to measure the free chlorine content in water [3]. Electrochemical methods have shown to be a good alternative for the analysis of different inorganic and organic species due to their sensitive and rapid response, in addition to their simplicity and their possible on-line operation [14]. In particular, amperometry and potential sweep techniques have been extensively involved in the direct determination of free chlorine using its electrochemical oxidation or reduction properties [15–23]. The

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type of electrode materials used for chlorine analysis include platinum [19,21–25], gold [26,27], glassy carbon [15], graphite [16], CNT composite electrodes [21], poly-melamine modified electrodes [28], AuNPs/PEDOT nanocomposite [29] and poly MnTAPP-nano Au film modified electrodes [30]. However, the determination of free chlorine using inkjet printed silver electrodes has not been reported to date. Stripping voltammetry for chlorine analysis by a system using a silver electrode was mentioned in the patent literature, but no results were shown without clear explanation of the working principle and of the employed apparatus [31]. Recently, inkjet printing of functional devices has attracted a much attention as demonstrated by a growing number of applications, such as the fabrication of disposable, cost-competitive sensors with fast response and low detection limits [32–35].

Although widely used as reference electrode material in electrochemistry, silver is not often used as a working electrode because of its small potential window and chemical lability. Despite these facts, silver still holds advantages for electrochemical studies such as its relatively low price compared to the other noble metals, and, in the present study, its reactivity with chlorinated species and the possibility to prepare reproducible silver electrodes by inkjet printing. Similar approach was mentioned in the study by da Silva et al. [36] for manufacturing Ag/AgCl reference electrodes. The main advantages of using inkjet printed silver electrodes over regular silver electrodes are the following: i) the inkjet printed electrodes are disposable and less expensive than common silver electrodes due to the smaller amount of silver employed, ii) a highly reproducible response can be achieved among different electrodes thanks to the fact that the electrode area is precisely defined by the inkjet printing processes, iii) the fabrication of Ag electrodes by inkjet printing is very flexible in terms of scalability simply by modifying the desired dimensions and geometries in the digital pattern files, and iv) a broad range of solid and flexible substrates is available. These advantages enable the rapid, reliable and affordable production of single or multiplexed, portable and easy-to-use sensors. Herein, an easy-to-perform electrochemical method for the analysis of free chlorine in aqueous media based on the spontaneous reaction of free chlorine with an inkjet printed silver electrode is presented. The presence and concentration of free chlorine species are thus transduced at the silver electrode in the form of an AgCl/Ag₂O film that can be quantitatively analyzed by linear sweep voltammetry (LSV). Silver electrodes were printed on flexible polyimide substrates, allowing for small and portable sensing systems for the analysis of free chlorine in forensic, swimming pool or industrial water samples. After optimization of different parameters, lowest detectable free chlorine concentration was 0.4 ppm (by approximation of calibration curve to $y = 0$), while the limit of detection ($S/N = 3$) was equal to 2 ppm, with a sensitivity of 30 $\mu\text{C/ppm}$.

2. Experimental Part

Potassium dihydrogen phosphate (KH_2PO_4) was purchased from Sigma Aldrich, disodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) from Fischer Scientific and sodium hydroxide (NaOH) from Fluka. Sodium hypochlorite solution (NaClO, available chlorine 5%) was obtained from ACROS OrganicsTM. All chemicals used were of analytical reagent grade. Aqueous solutions were prepared using ultra pure deionized water (Millipore, 18.4 M Ω cm). Buffer solutions of KH_2PO_4 -NaOH (50 mM, pH 5.8), KH_2PO_4 -NaOH (50 mM, pH 8) and $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (50 mM, pH 9) were employed as supporting electrolytes. For the validation of the proposed methodology, commercial disinfectant *Eau de Javel* (2.5% NaClO) and water sample from swimming pool in Lausanne, Switzerland were used and kept in a dark and cold place prior to its analysis. The pH was measured with a conventional pH meter (Metrohm 744). For the readout of the N,N-diethylparaphenylenediamine (DPD) spectrophotometric method, a UV-Visible ChemStation from Agilent Technologies was used.

2.1. Inkjet Printing of Silver Working Electrodes

Silver working electrodes were prepared by using a drop-on-demand inkjet printer (DMP-2831 Dimatix Fujifilm, Santa Clara, CA, USA) and a disposable cartridge (DMC11610 Dimatix Fujifilm, Santa Clara, CA, USA) containing 16 individually addressable nozzles with nominal droplet volumes of 10 pL. All silver patterns were printed over a Kapton HN foil substrate (polyimide (PI); 125 μm -thick; Goodfellow, Huntingdon, England) using a commercial silver ink (EMD5603, Sunchemical, Carlstadt, USA). During printing of the silver layer, the substrate temperature was set to 60 °C in order to promote evaporation of the ink carrier and thus to increase the pattern resolution. After printing, Ag patterns were cured for 30 min at 200 °C with a heating and cooling rate of 1–2 °C/min. Afterwards, an insulating layer was printed over the silver pattern to precisely define the active area of the silver electrode (*i.e.* surface 4 mm², Fig. 1). The insulating UV curable ink (EMD6101, Sunchemical, Carlstadt, USA) was simultaneously polymerized by UV exposition with a light guide connected to an Omnicure S2000 mercury UV lamp (Lumen Dynamics, Mississauga, Ontario, Canada) and mounted on the DMP-2831 print head. Printing parameters (cleaning steps, cartridge temperature, waveform, jetting frequency, number of nozzles, etc.) were optimized for both employed inks. Electrical connections were checked with a multimeter, while dimensions and physical characteristics of the printed patterns were investigated by laser-scanning microscopy (LSM) in reflection mode using a Keyence VK 8700 (Keyence, Osaka, Japan). Further characterization of the inkjet printed electrodes before and after the electrochemical detection of free chlorine was performed by high resolution scanning electron microscopy (HR SEM, Merlin Zeiss, Germany) equipped with a Gemini II column and a secondary electron, in-lens detector. Finally, the chemical composition of the AgCl/Ag₂O film surface was investigated by X-ray Photoelectron Spectroscopy, XPS (ESCA KRATOS AXIS ULTRA).

2.2. Electrochemical Detection of Free Chlorine with Silver Printed Electrodes

A 500 ppm free chlorine standard solution was prepared by dilution of a 5% aqueous NaClO stock solution. Other solutions with lower concentrations were freshly prepared by dilution of the 500 ppm standard solution and using a specific pH buffer solution. All solutions were kept in the dark, transported in brown glass bottles and stored at 4 °C. Analyzed free chlorine solutions were in the range from 1 to 100 ppm. Experiments were performed in air at atmospheric pressure conditions and at 21 ± 2 °C. Electrochemical measurements were carried out in a single compartment cell containing a Ag/AgCl (1 M KCl) reference electrode, a platinum wire counter electrode and the inkjet printed silver working electrode. All measurements were performed in a total volume of 10 mL of sample solution. The linear sweep voltammetry (LSV) experiments were carried out with an Autolab potentiostat (PGSTAT128N, Utrecht, Netherlands). The quantification of free chlorine proceeded as follows (*vide infra*): 1) electrode preconditioning, in order to have a completely clean and reduced surface of silver electrode; 2) formation of AgCl/Ag₂O as a result of the reaction between the silver electrode and the present free chlorine, 3) replating of silver and transduction of the voltammetric signal into the free chlorine concentration.

3. Results and Discussion

3.1. Characterization of Inkjet Printed Electrodes

As described above, the silver patterns were constituted of a small square (4 mm²) linked to a rectangle (20 mm \times 1 mm) employed for the electrical connection. A UV curable insulating ink pattern was printed along the rectangle (12 mm \times 2 mm) to precisely define the square of active electrode area (Fig. 1b). As seen on the SEM images

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