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On-chip electrochemical microsystems for measurements of copper and conductivity in artificial seawater.

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Abstract: The fabrication and characterisation of microelectrochemical sensors for Cu^{2+} and conductivity suitable for operation in the marine environment are presented. The impact of the designs on sensor performance and their adequacy to operate in real conditions are discussed. The sensors, tailored to voltammetric and impedimetric measurements, are fabricated on silicon using photolithographic and thin film deposition techniques. The impedimetric sensor is made of Pt interdigitated electrodes which are used for the measurement of conductivity. The voltammetric sensors are based on a three electrode electrochemical cell with on-chip Ag|AgCl reference and Pt counter and working electrodes, used for detection of copper by underpotential deposition – stripping voltammetry at microelectrode array. The sensors operated in the Cu²⁺ concentrations ranging from 0.48 to 3.97 μ M with a limit of detection of 0.115 μ M. The impact of the temperature, the pH and the salinity of the artificial seawater on the sensitivity for Cu²⁺ detection are also considered. Measurements of copper concentration and conductivity are validated using certified reference materials and standard solutions.

Introduction

Electrochemical methods are of particular interest for in-situ environmental applications as operating procedures remain simple and are without or with limited sample pre-treatment, which is essential for their implementation outside the laboratory. Miniaturised electrochemical sensors offer a number of advantages over macroscopic electrodes including (i) improved mass transport and hence increased sensitivity (due to the hemispherical diffusion); (ii) improved signal to noise ratio; (iii) reduced *iR* drop [1]. Thus, microfabricated electrochemical sensors can provide sufficient sensitivity and achieve required limits of detection for practical applications due to improved mass transfer and signal to noise ratio. A number of miniaturised electrochemical sensors for autonomous in-situ measurements have been developed [2–9]. Autonomous electrochemical systems were devoted to the detection of heavy metals in sea water by either cathodic stripping voltammetry [2,3] (CSV) or anodic stripping voltammetry [4–7] (ASV). Concentration of dissolved oxygen in seawater has also

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