Cu-DOPED POLYMERIC-MODIFIED ELECTRODE FOR DETERMINATION OF CYSTEINE

C. A. MARTÍNEZ-HUITLE[†,ǂ], C. CARLESI JARA[ǂ], M. CERRO-LOPEZ[‡] and M. A. QUIROZ[‡]

† *DiSTAM, University of Milan, via Celoria 2, CAP-20133 Milan, Italy.*
ǂ*Universidade Federal do Rio Grande do Norte, Centro de Ciências Exatas e da Terra. Departamento de Química, Lagoa Nova CEP 59078-970 - Natal, RN, Brasil mhuitle@hotmail.com, carlos.martinez@unimi.it*
ǂ *Escuela de Ingeniería Química, Pontificia Universidad Católica de Valparaíso. Avda. Brasil 2147, 2362804 Valparaíso, Chile. carlos.carlesi@ucv.cl*
‡ *Universidad de las Américas – Puebla. Departamento de Química y Biología, Laboratorio de Electroquímica, CP 72820 – Puebla, México. marcoa.quiroz@udlap.mx*

***Abstract*— A simple differential pulse voltammetric method based on chitosan modified glassy carbon was used to pre-concentrate copper ions in the chitosan film. After, this electrode was employed for the quantitative determination of cysteine. The modified electrode exhibits a clear improvement of the current response. The method allowed quantifying the analyte in the range in buffer solution and a limit of detection range from 1.0×10^{-6} to 1.4×10^{-6} M was achieved. This value seems quite higher than those previously published by other authors. The results are described and discussed in the light of the existing literature.**

***Keywords*— cysteine, sensor, chitosan, copper.**

I. INTRODUCTION

Cysteine is a naturally occurring amino acid of great importance in biological and biomedical fields. It participates in a number of biochemical processes, and is involved in several important cellular functions, such as protein synthesis, detoxification and metabolism. Cysteine is also important in food science, being widely used as antioxidant in a large variety of foods (Friedman, 1994; Elias *et al.*, 2005; Koh *et al.*, 1996).

Several methods have been described for quantifying cysteine in a variety of real matrices, including spectrophotometric (Zaia *et al.*, 1999; Rozhnova *et al.*, 1999), fluorimetric (Wang *et al.*, 2001; Zhu *et al.*, 2003), electrophoretic (Zeng *et al.*, 2006; Jin and Wang, 1997) mass spectroscopy (Raftery *et al.*, 1992) and chromatograpic (Amarnath *et al.*, 2003; Brückner *et al.*, 1995) ones.

Electrochemical methods were also described since offering high sensitivity and selectivity (Jin and Wang, 1997; Forsman, 1981 and 1983; Van den Berg *et al.*, 1988; Sugawara *et al.*, 1996; Heyrowský *et al.*, 1997; Kawasaky *et al.*, 1999; Amini *et al.*, 2003). These papers deal with the behavior of cysteine at mercury electrodes (Heyrowský *et al.*, 1997), at gold-mercury amalgam electrodes (Jin and Wang, 1997), at electrodes in the presence of Co(II) (Sugawara *et al.*, 1996; Amini *et al.*, 2003), at thin mercury film electrodes in the presence of osmium (Kamiński and Modrzejewska, 1997), gold nanoparticle-modified electrodes (Agüí *et al.*, 2007), amperometric detection (Tseng *et al.*, 2006) and at mercury electrodes in the presence of Cu(II) (Forsman, 1981 and 1983; Van den Berg *et al.*, 1988). According to these last papers, the reactions involved, in particular, the reaction of cysteine with Cu(II) to give a cuprous cysteinate complex and cystine can be exploited for quantifying cysteine by differential pulse cathodic stripping voltammetry. In this respect, Forsman (1981) reported that the calibration curve obtained in the presence of 10^{-5} M Cu(II) was linear in the 2×10^{-9} – 5×10^{-7} M range.

In the course of some investigations on the electrochemical properties of chitosan-modified (Ct-GC) electrodes, it was observed that they exhibit a high permselectivity towards Cu(II) ions (Kamiński and Modrzejewska, 1997; Schmuhl *et al*., 2001; Martinez-Huitle *et al.*, 2006). This strong affinity between Cu and chitosan film was ascribed to the presence of two ligands around each metal ion (Kamiński and Modrzejewska, 1997; Schmuhl *et al.*, 2001), as described in Fig. 1. Then, it seemed interesting exploring the possibility of quantifying cysteine at chitosan-Cu(II) modified glassy carbon (CtCu-GC) electrodes. This paper reports the results of some preliminary measurements.

II. METHODS

A. Chemicals

Chemicals were of the commercially available highest quality and were used without further purification. Chitosan was purchased from Aldrich. The other reagents were purchased from Fluka. Aqueous solutions were prepared using double-distilled deionised water and purged with nitrogen gas prior to each experiment.

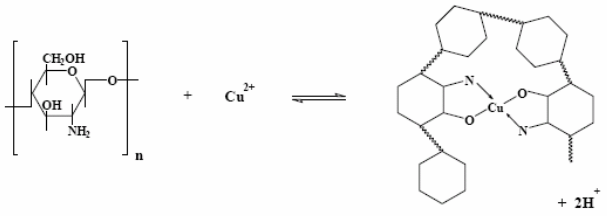

Fig. 1: Chemical structure of coordination between metal ion (Cu(II)) and Ct.