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Fast Direct and Indirect Determination of Se (IV) at Gold Ultramicroelectrode in Flow injection analysis Using Fast Fourier Transform Square Wave Voltammetry

Parviz Norouzi[1?î], M. Sheikhynejad[1], and G. Vatankhah[2]
[1] *University of Tehran, Department of Chemistry, Faculty of Science,*
[2] *Iranian Research Organization for Science and Technology (IROST), Isfahan*
E-mail: Norouzi@khayam.ut.ac.ir

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Abstract

Electrochemical (EC) data, in particular, when the magnitude of current is in range of nano and pico ampere, suffers from existence of environmental noises. In this work, a new modified SW voltammetric method for determination of Se(IV) is presented. Where signal-to-noise ratio has significantly (near to 620 times) increased by application of discrete Fast Fourier Formation (FFT) method, background subtraction and two-dimensional integration of the electrode response over a selected potential range and time window. Also, the detection method can be used for direct and indirect determination of Se(IV) ions by measuring the changes in SW voltammogram (or admittance) of an gold ultramicroelectrode (in 0.05 M H_3PO_4 solution) caused by redox reaction or just adsorption of the Se(IV) ion on the electrode surface. In indirect detection, the analyte signal was calculated based on admittance changes related to inhibition of oxygen adsorption (by adsorbed of Se(IV) ions). Direct measurement was carried out on an anodic stripping mode, after accumulation of the analytes on the electrode surface for 50 to 100 ms. In method, removal of oxygen from the studied solutions is not required. Calibration plots are given for solutions containing 10^{-8}–10^{-7} M and 10^{-7}–10^{-6} M of Se(IV) The limit of detection is calculated to be 2.5×10^{-9} M. The relative standard deviation at concentration 3×10^{-8} M is 6 % for 5 reported measurements.

Keywords: *Fast Fourier Transformation, Square wave voltammetry, Gold ultramicroelectrode, Flow-injection, Selenium*

Introduction

In environment, inorganic forms of selenium exist in various oxidation states; elemental selenium (Se^0), selenide (Se^{2-}), selenite (Se(IV)), and selenate (Se(VI)) (Bowen, 1979 and Bagnall, 1966). The Se(IV) and Se(VI) forms are both commonly found in natural waters, but of the two species, Se(IV) is the more highly toxic (Clayton & Clayton,1982). There are currently several laboratory-based analytical techniques used to analyze Se(IV)in various matrices (Saraswati *et al.*, 1995). Research in effects of selenium in environment requires measurement of widely different selenium concentrations in many types of biological samples (blood, hair, urine, muscle, etc.) and in a variety of food stuffs (Watkinson, 1966 and Lockitch *et al.*,1989).

Electroanalytical techniques, especially stripping voltammetry, not only offer the advantages of high sensitivity and low cost, but also due to simple instrumentation, can be easily utilized for analysis. In the past, several voltammetric stripping methods have been extensively applied in studying selenium in various aqueous matrices. These have included adsorptive, and (cathodic or anodic) stripping voltammetry (ASV), (Tan & Kounaves, 1998 and. Rurikova & Kunakova, 1999). In order to determine total Se, all forms of the selenium must first be converted to Se(IV). This is because, Se(IV)is the only electroactive form and can be easily analyzed by stripping voltammetry (Binski, 2000).

In general, there have been several approaches to decrease detection limits in voltammetric measurements (Vydra *et al* 1976 and. Brainina & Neyman, 1993). Where, a careful attention to the sources of unwanted currents in construction led to improvement of signal-to-noise (S/N). For example, the charging current significantly can be reduced by reducing of surface area of the working electrode. Indeed, in recent years, the use of voltammetric techniques has been further stimulated by the advent of ultramicroelectrodes (UMEs) (Feeney & Kounaves, 2000; Murray 1984 and Budnikov *et al*, 1994). Also, electronic or digital filters have been used for elimination or reduction of noise (Feeney & Kounaves, 2000). In principal, it is possible to combine some of these approaches to yield even greater improvements. For example, mathematical manipulation of the data can be very promising in determination and elimination of noise and enhancement of analyte signal.

The combination of UME with Square wave voltammetry (SWV) has recently been shown to be advantageous for environmental detection of several metals (Yu-Chen Tsai, *et al.*, 2001). The adaptation of this technology to ASV of Se(IV) on a gold UME could provide a substantial improvement for rapid analysis (Tan & Kounaves, 1998 and Rurikova & Kunakova, 1999). This paper describes a fundamentally different approach to SWV measurement, in which the detection limits are improved, while preserving the information content of the SW voltammogram. The approach is designed to separate the voltammetric signal and background signal in frequency domain by using discrete Fast Fourier Transformation (FFT) method. This separation allows, digitally filtrating some of the noises and decreasing the bandwidth of the measurement. Further improvement in the signal was gained by two-dimensional integration of the electrode response over a selected potential range and time window of the signal.

Experimental

Reagents

All solutions were prepared in double-distilled deionized water (Corning Mega-Pure System, MP-6A and D-2) using analytical grade reagents. Reagents in use in preparation of the stock eluent solution for flow-injection analysis (0.05 M H_3PO_4 and NaOH 1M used for adjusting pH of the eluent) were obtained from BDH Chemicals. In all experiments all solutions were made up in the background electrolyte solution, and were used without removal of dissolved oxygen.

Flow Injection Setup

The equipment for flow injection analysis included a 10 roller peristaltic pump (Microperpex) and a four–way injection valve (Supelco Rheodyne Model 5020) with a 50 μl sample loop. Solutions were introduced into the sample loop by means of a plastic syringe. The electrochemical cell used in flow–injection analysis is shown in Figure 1. In all experiments, described in this paper, the flow rate of eluent solution was 2.0 mL/min.

Electrode preparation

Gold ultramicroelectrodes (12.5 and 5 μm) were prepared by sealing metal micro-wires (Goodfellow Metals Ltd., UK) into a soft glass capillary. The capillary was then cut perpendicular to its length to expose the wire. Electrical contacts were made using silver epoxy (Johnson Matthey Ltd., UK). Before each experiment the electrode surface was polished for 1 minute using extra fine carbon paper and then for 10 minutes with 0.3 μm alumina. Prior to being placed in the cell the electrode was washed with water. In all measurements an Ag(s)|AgCl(s)|1M KCl(aq) reference electrode was used. The auxiliary electrode was made of a Pt wire, 1cm length and 0.5 mm in diameter.

Electrochemical Setup.

All electrochemical experiments were done using a setup comprised of a PC PII Pentium 233 MHz microcomputer equipped with a data acquisition board (PCL-818PG, PC-Labcard Co.) and a custom made potentiostat. The potential waveform consisted of two sections; a) electrode conditioning and b) measurement (see Fig. 2). The electrode conditioning started with cleaning process, in which the electrode potential was held at a positive potential E_c, and then followed with accumulation of the analyte at potential E_a.

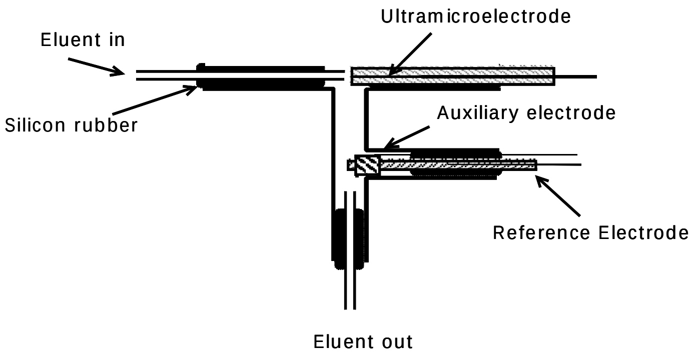

Figure 1 - Electrochemical cell used in Flow-Injection experiments.