

Pulsed amperometric detection of sulfide, cyanide, iodide, thiosulfate, bromide and thiocyanate with microfabricated disposable silver working electrodes in ion chromatography

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Received 27 October 2004; received in revised form 15 December 2004; accepted 15 December 2004

Available online 19 January 2005

Abstract

The authors introduce a new type of silver electrodes. The new electrodes are designed to be disposable and as such they are used only for a limited period of time, usually 5–7 days, and then discarded. Manual polishing, which is required with non-disposable electrodes, is not necessary with disposable electrodes. This manuscript describes the development of pulsed amperometric detection waveforms that make it possible to utilize disposable silver electrodes in the chromatographic detection of sulfide, cyanide, iodide, thiosulfate, bromide and thiocyanate. Also discussed is an evaluation of analytical performance of the electrodes with the newly developed waveforms. The detection limits were found to be 1 ppb (S^{2-}), 2 ppb (CN^{-}), 5 ppb (Br^{-} , $S_2O_3^{2-}$ and I^{-}) and 10 ppb (SCN^{-}) for a 10 μ l injection volume. Calibration plots for S^{2-} , CN^{-} , Br^{-} and $S_2O_3^{2-}$ are linear from their respective detection limits up to 50–100 ppm. The linear calibration for I^{-} and SCN^{-} can be obtained from the detection limits up to 10 ppm. Reproducible long-term performance was confirmed in a 2-week experiment with 10 μ l injections of 1 ppm CN^{-} .

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Keywords: Disposable electrodes; Thin film electrodes; Silver electrodes; Ion chromatography; Pulsed amperometric detection; Sulfide; Cyanide; Bromide; Thiosulfate; Iodide; Thiocyanate

1. Introduction

Electrochemical analysis of low concentrations of sulfide, cyanide, bromide, thiosulfate, iodide and thiocyanate has been of great importance in environmental, food and clinical samples. It is also playing an important role in the purity assays of chemical and pharmaceutical products [1–5]. Electrochemical methodologies for these anions range from amperometry [6,7] and polarography [8] to cathodic stripping voltammetry [1,3,4,9]. However, in all non-chromatographic methods, interferences from other analytes or from matrix constituents affect the quality of electrochemical results.

Rocklin and Johnson reported the first combined use of a chromatographic separation and an electrochemical detection technique [2]. Their combination of chromatography and dc amperometry on a silver electrode resulted in improved selectivity and increased sensitivity.

For more than 20 years, the detection of all inorganic anions by means of silver electrodes was performed at a constant potential. Over time, analysts became aware of the limitations of such an approach. Rohrer [10] reviewed known problems with dc amperometry of iodide on silver electrodes and introduced the first pulsed amperometric method for the ion chromatographic detection of that anion on silver electrodes. In another recent publication, Giuriati et al. [11] described the development of a pulsed amperometric technique that utilized silver electrodes for the ion chromatographic detection of sulfide and cyanide.

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At present, the prevailing convention applies the term pulsed amperometric detection (PAD) to all techniques that impose repeated changes of potentials (waveforms) and generate a signal by integrating the working electrode current over a very short time period, during which the applied potential remains unchanged. On the other hand, the term integrated pulsed amperometric detection (IPAD) is reserved for techniques that use waveforms with current integration periods extending over two or more different values of applied potentials.

The first example of PAD was introduced by Johnson and his group for alcohol analysis on platinum electrodes [12]. The first application of IPAD was reported for the detection of amino acids with gold electrodes [13].

It should be noted that the reports by Rohrer and Giuriati et al., showing the first examples of using PAD and silver electrodes, were generated with non-disposable (bulk) silver electrodes. To the best of our knowledge, there are no published reports describing a PAD detection with thin film silver electrodes; the PAD conditions in the existing two reports are not necessarily suitable for use with a micro-fabricated disposable electrode that has a working electrode metal thickness of only several hundred nanometers. Moreover, from the six inorganic anions known to be amenable to amperometric detection on silver electrodes, only three (CN^- , HS^- and I^-) have been successfully detected with PAD so far.

In this article, we discuss a development and optimization of waveforms for use with disposable thin film silver electrodes. The optimized waveforms are applied to the detection of six inorganic anions.

2. Experimental

2.1. Fabrication of disposable silver electrodes

The disposable silver electrodes were fabricated by a process similar to that used for the preparation of disposable gold electrodes. As reported previously [14], polyethylene naphthalate (Kaladex, DuPont, Wilmington, DE, USA) was found to give the best performance as a substrate material for disposable Au electrodes. The Kaladex films (0.125 mm) were cleaned of particles by blowing them off with filtered nitrogen gas. Next, they were rinsed with 18 M Ω water and methanol. A ca. 500 Å titanium layer was deposited onto the pre-cleaned substrate by radio frequency sputtering, which promotes the adhesion of the silver films. The silver layer was then prepared by radio frequency sputtering onto the titanium layer formed in the preceding step. The total thickness of the silver layer was ca. 6000 Å. The purity of the utilized silver target was 99.99%. A special mask defining the electrode pattern was applied for both the titanium and silver deposition steps.

The resulting sheets, each holding 24 silver electrodes, were cut into individual electrodes. Two alignment holes were punched into each electrode for a precise installation into the ED 50 electrochemical detection cell (Dionex, Sunnyvale,

CA, USA). The geometric area of the working electrode was 0.785 mm² (circular electrode, 1 mm diameter).

2.2. Anion-exchange chromatography and PAD detection

All experiments were performed with a BioLC liquid chromatography system (Dionex). The system consisted of a GP 50 gradient pump with on-line degassing, an AS 50 autosampler (injection loop 25 μl), and a column set consisting either of an analytical column IonPac[®] AS15 (2 mm \times 250 mm) with a pre-column IonPac AG15 (2 mm \times 50 mm) or analytical column IonPac AS16 (2 mm \times 250 mm) with a pre-column IonPac AG16 (2 mm \times 50 mm). The pre-column and column were placed in an LC30 column thermostat set at 30 °C. The column outlet was connected to an ED 50 electrochemical detector cell. An Ag/AgCl (3 M KCl) electrode was chosen as a reference electrode, while the titanium cell body was used as a counter electrode. The disposable electrode was mounted against the detector cell body using a holder block and two wing nuts. The detailed set-up of the ED 50 electrochemical cell is described in Ref. [14]. The cell gasket dimensions were as follows: thickness, 0.051 mm; flow channel, 1.2 mm \times 8 mm.

The chromatographic system control, data acquisition and analysis were carried out with the help of PeakNet 6.5 software (Dionex). The starting point of the detection method optimization was with a waveform reported in Ref. [10].

All separations were carried out at a flow rate of 0.25 ml/min with an isocratic mobile phase containing 62.5 mM NaOH. The eluent was maintained under helium or nitrogen to prevent entry of atmospheric carbon dioxide. The IonPac AS15 column set (guard 2 mm \times 50 mm, analytical 2 mm \times 250 mm) was utilized for separations of sulfide, cyanide, bromide and thiosulfate; the IonPac AS16 columns of the same dimensions were used for separations of iodide and thiocyanate. All chemicals were of reagent grade purity or better, and were used without further purification.

2.3. Preparation of standards and samples

If a standard or sample contains sulfide only, DI water can be used to make final dilutions. With a cooled autosampler sample tray set at 5–10 °C, sulfide can be kept stable for up to several days. However, when standards or samples were stored longer than 2–3 days, even at low temperature (i.e., in a refrigerator), we observed a new peak in the chromatogram of sulfide samples that we attributed to the formation of a polysulfide. If a standard or sample contained cyanide, we prepared dilutions in 0.25 M NaOH. The cyanide was then stable for 2–3 days even at room temperature. However, if cyanide and sulfide required a simultaneous quantitative determination, cooling the autosampler sample tray became necessary in addition to the use of 0.25 M NaOH as a sample matrix.

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