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Electroanalysis of Organic Compounds at Bismuth Electrodes: A Short Review

Nikolitsa Lezi[1], **Vlastimil Vyskočil**[2], **Anastasios Economou**[1]*, and **Jiří Barek**[2]

[1] *Laboratory of Analytical Chemistry, Department of Chemistry, University of Athens, 157 71 Athens, Greece*

[2] *UNESCO Laboratory of Environmental Chemistry, Department of Analytical Chemistry, Faculty of Science, Charles University Prague, Hlavova 2030/8, 128 43 Prague 2, Czech Republic*

Abstract: Over the last twelve years, it has been demonstrated that bismuth electrodes have comparable electroanalytical performance to mercury electrodes in the negative potential range. Since the toxicicty of bismuth is lower than that of mercury, bismuth can serve as an alternative "green" electrode material to mercury. However, the great majority of published work at bismuth–based electrodes is concerned with the determination of trace metals by voltammetric techniques with only few applications dealing with the electroanalysis of organic compounds. This work is a review of the field of electroanalysis of organic species at bismuth electrodes. The review covers the different types of bismuth electrodes used for various classes of target organic species that are electroactive at bismuth electrodes and within the electrochemical detection schemes used in conjunction with bismuth-based electrodes.

Keywords: Organic compounds; Electroanalysis; Bismuth electrodes.

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*) Author to whom correspondence should be addressed. E-mail: aeconomo@chem.uoa.gr

Introduction

Bismuth electrodes, introduced in 2000 for electroanalytical purposes [1], have gained increasing popularity over the last few years. Due to the low toxicity of bismuth, this "green" metal can serve as a substitute electrode material for mercury in electroanalysis. In most respects, bismuth electrodes exhibit similar electroanalytical performance to mercury (with

the exception of a more restricted anodic polarisation range) while the fact that bismuth is solid at room temperature (in contrast to mercury) imparts great flexibility in the fabrication of bismuth-based sensors. The field of electroanalysis on bismuth electrodes has been reviewed previously and the existing reviews have revealed that bismuth electrodes are dominated by applications involving trace metal analysis with electrochemical stripping methods [2–5]. However, despite the fact that bismuth is an attractive electrode material for the determination of reducible organic compounds due to its high cathodic overpotential window, there are relatively few applications in this area.

The present review is focused on the application of bismuth-based electrodes in organic electroanalysis and aims to present the potentialities of these sensors for the determination of organic compounds. The review covers the different types of bismuth electrodes used for organic electroanalysis (bismuth-film electrodes, bismuth-bulk electrodes, bismuth-nanoparticle modified electrodes), the various classes of target organic species that are liable to electroanalysis at bismuth electrodes (pesticides, nitro-compounds, azo-compounds, biologically active molecules) and the diverse electrochemical detection schemes used in conjunction with bismuth electrodes.

Types of Bismuth Electrodes for Organic Electroanalysis

The simplest bismuth electrode for organic electroanalysis is the bismuth–bulk electrode (BBE). This is fabricated from a commercial bismuth rod embedded in an insulator [6] or by moulding melted bismuth in a cylindrical glass tube to form a rod [7,8]. The advantages of this type of sensor are the ease of fabrication, the easy and rapid surface regeneration (by simple polishing) and the relative homogeneity of the electrode surface.

Bismuth–film electrodes (BiFEs) are normally fabricated by *in situ* or *ex situ* electroplating a thin bismuth film on the surface of a conductive support. *In situ* plating is only suitable for the analysis of trace metals by anodic stripping voltammetry which involves cathodic electrolysis step. Therefore, all reported applications of BiFEs in organic electro-analysis utilize preplating of the substrate from a separate plating solution containing Bi(III) in acidic media to avoid hydrolysis of the metal cation. The plating conditions are variable: the Bi(III) concentration in the plating solution ranges from a few mg L^{-1} [9] to a few thousands of mg L^{-1} [10] with typical Bi(III) concentrations being between 50 and 500 mg L^{-1} [e.g. 11–13]. The supporting electrolyte is normally an acid [14,15] or acidic buffer solution

[12,16,17]. The presence of KBr has been shown to improve the adherence of the bismuth film on the electrode surface [18,19].

The bismuth plating potential is normally less negative than –0.6 V although underpotential deposition in the range +0.1 to –0.3 V has also been reported [20–22]. Finally, the plating time ranges from as low as 60 s [9,19] to a few minutes [23,24].

On the other hand, different materials have been employed as supports for the generation of the bismuth film: copper [22,25,26], solid silver amalgam [23], glassy carbon [11,13–16,18,19,24,27–31], mesoporous platinum microelectrodes [20,21], carbon paste [8,17,24,29,32], pencil lead [12,33] and screen–printed carbon inks [34]. Flow–through cells equipped with BiFEs on glassy carbon and carbon paste have also been reported [9,10,35]. In this case, the bismuth plating and stripping steps were conducted on-line: a Bi(III) solution was directed to the cell while applying a negative potential at the working electrode to generate a bismuth film. The film was also potentiostatically cleaned at an anodic potential in flowing solution [9,35]. The advantages of BiFEs are the possibility for efficient regeneration of the electrode surface by removing the used film but the surface homogeneity of the electrode surface is rather variable and dependent on the plating conditions.

Bismuth–based electrodes modified with bio-recognition agents (enzymes, antigens) have also been reported [34,36–38]. Screen–printed ink, carbon paste and glassy carbon are the substrates used for these biosensors. The modification strategies range from simple spread–coating of the electrodes with bismuth nanoparticles and enzymes, to immobilizing the enzymes in polymeric membranes and, finally, to *in situ* entrapment of enzymes during bismuth deposition.

Detection Techniques

In most applications involving the determination of toxic organic compounds and drugs at bismuth–based electrodes, solution–phase voltammetry has been utilized as the detection technique. Cyclic voltammetry [6,9,19–21] and linear sweep (DC) voltammetry [23] have been used occasionally. However, pulse techniques are the commonest with the view to achieve low limits of detection due to their capacity to minimize the non-faradaic current components. The differential pulse (DP) modulation is the most frequently used [7,11,12,15, 18,22,23,27,29,31,39] and followed by the square wave (SW) mode [9,24,28,30,40].

Even lower detection limits can be achieved with the use of stripping voltammetry. In this case, the voltammetric scan is preceded by a preconcentration step of the analyte on the

working electrode. In most cases, adsorptive preconcentration as highly effective pre-concentration step was utilized in combination with cathodic scanning that followed and enabled reduction of the accumulated species [7,8,16,26,32,33], but electrolytic pre-concentration combined with an anodic scan for oxidation of the target species has found some limited applications [14,25,41].

Biosensors are inherently selective due to the incorporation of a biologically active agent (enzyme or antigen) specific to the target analyte. In this case, DP voltammetry [36] or simpler detection techniques (mainly chronoamperometry) can be used for the detection of mediators or enzymatic reaction products [7,10,34,37,38,42]. Amperometric detection is also normally employed in flowing streams [9,35].

Survey of Applications

Determination of Toxic Compounds

The majority of applications of bismuth electrodes in organic electroanalysis involves different classes of toxic compounds. These can be detected by solution–phase voltammetry (DC, DP or SW), adsorptive stripping voltammetry or amperometry.

Amongst them, different aromatic nitro–derivatives lend themselves to direct cathodic voltammetric analysis. A BBE electrode was used to determine mononitrophenols, dinitro-phenols, nitrobenzoic acid and nitrobenzaldehyde [6,7]. Nitrophenols were additionally detected at a flow–through cell equipped with a glassy carbon working electrode preplated with a bismuth film [9]. 2,4–Dinitrophenol in spiked water samples was determined at a glassy carbon support plated *ex situ* with a bismuth film [11]. 2–Amino–6–nitrobenzothiazole has been determined in spiked tap water and mineral water by differential pulse and DC voltammetry at a silver–mercury amalgam electrode covered *ex situ* with a bismuth film [23]. 2–itrophenol and 4–nitrophenol were detected at an *ex situ* plated BiFE on pencil–lead and their responses were resolved using a chemometric approach [12]. Finally, nitrobenzene was detected in spiked water samples at a preplated bismuth–film carbon paste electrode in the presence of cetyltrimethylammonium bromide [32].

Pesticides are also liable to analysis at bismuth–based electrodes. Paraquat and atrazine have been detected in spiked water samples at copper electrodes preplated with bismuth films [22,26]. BiFEs preplated on glassy carbon have been employed to determine

various other pesticides (herbicides, thiamethoxam, imidacloprid, acetamiprid, nitenpyram, metamitron, clothianidin, thiamethoxam) [18,19,24,29].

Carbon paste electrodes preplated with a bismuth film were used for the determination of herbicides and isecticides [24,28,29]. Finally, parathion could also be determined at the BBE [7]. Azo-dyes have been determined in beverages at a glassy carbon electrode covered with a bismuth film [15] or modified with poly(*p*–aminobenzene sulfonic acid) before being covered with a bismuth film [39].

Determination of Pharmaceuticals and Drugs

Vitamin B12 has been determined at a BiFE preplated on a copper substrate by SW anodic stripping voltammetry [25]; the target analyte was preconcentrated as Co(II) onto the electrode followed by reoxidation of Co(II) to Co(III) by an anodic scan. The method was used to determine vitamin B12 in pharmaceuticals.

Sildenafil, colchicine, aminosalicylate drugs and sulfathiazine have been determined in pharmaceutical preparations on glassy carbon electrodes preplated with a bismuth film [16,27,30,31]. A flow–through cell incorporating a tubular carbon paste electrode coated with a bismuth film in the *ex-situ* mode was used for the amperometric determination of the anti-biotic diclofenac in pharmacutical products [35]. Daunomycin (an anthracycline antibiotic for cancer chemotherapy) was determined at a BBE by SW adsorptive stripping voltammetry [8].

Finally, a glassy carbon electrode modified with Bi_2O_3/multi–wall carbon nanotubes has been reported for the determination of cilostazol (used for the treatment of intermittent claudication and stroke prevention) in pharmaceuticals and spiked human plasma by SW anodic voltammetry but the utility of the presence of the Bi_2O_3 has not been discussed in view of the oxidative range used [40].

Determination of Biologically Significant Organic Compounds

Abscisic acid (a phytohormone) was determined by SW adsorptive stripping voltammetry at a bismuth–coated pencil–lead electrode [33].

Metallothioneins (a group of proteins that contain metal atoms and have important biological and environmental roles in the metabolism and detoxification of some metals (Zn, Cd, Cu, Hg)) can be indirectly determined by DP anodic stripping voltammetric measurement of the metal cations they carry at a BiFE plated on glassy carbon [14]. A flow-through cell

featuring a BiFE preplated on a glassy carbon support was used for the determination of *Escherichia coli* by flow injection analysis (FIA).

The method was based on the release of β–D-glucuronidase from the bacterial cells in the culture medium that catalyzed the hydrolysis of the substrate 4-nitrophenyl–β–D-glucuronide to produce 4–nitrophenol; the culture medium containing the generated 4-nitrophenol was injected into the FIA manifold and 4-nitrophenol detected amperometrically at the BiFE [10].

Biosensors for two α–glucosidase inhibitors (amaryl and acorbose which are important in noninsulin–dependent diabetes mellitus) have been developed by immobilizing α-glucosidase on a bismuth–coated glassy carbon electrode using gelatin [37]. 4-Nitrophenyl–D–glucopyranoside was used as an enzymatic substrate and the liberated 4-nitrophenol was measured by chronoamperometry. The same design principle was used to construct a glucose biosensor for analysis of wines by immobilizing glucose oxidase on a preplated BIFE at a glassy carbon support using gelatin [38]; the oxidation of a suitable mediator (*Neutral red*) was followed by chronoamperometry.

Carbon paste electrodes modified with bismuth and biorecognition elements (enzymes and antibodies) have been fabricated [17,36]. For this purpose, a novel strategy of immobilization of the biological agents was developed in which the electrode was placed in a bismuth plating solution that, in addition to Bi(III), contained the bio-recognition element. During reduction of Bi(III), the the biological agent was entrapped within, or deposited on, the electrode surface. This modification approach was applied to the determination of xanthine in beverages using xanthine oxidasase and chronomaperometric detection of oxygen (mediator) [17] and as a sensing platform to study IgE and anti-IgE interactions using the voltammetric oxidation of neutral red as a reporter method [36].

In a similar fashion, screen–printed electrodes were modified with a bismuth film and a mushroom tissue for phenol detection [34]. In this case, the chronoamperometric response was obtained at a working potential of +800 mV; normally such a positive potential would cause oxidation and stripping of the bismuth film but in this case this was prevented and this phenomenon was attributed to the formation of a stable complex between Bi–film and the mushroom tissue should have been formed. In view of its response to phenol, it was speculated that polyphenol oxidase was the active enzyme in this biosensor.

A biosensor specific to phenols was fabricated by spread-coating a screen printed electrode with bismuth nanoparticles and tyrosinase (which catalyzes the oxidation of phenols to *o*–quinone). The generated *o*–quinone was amperometrically detected by its reduction to catechol at the electrode surface [42]. Glucose could then be determined *via* its oxidation at a

mesoporous Pt-electrode modified with bismuth [21]. Also, a multi–wall carbon nanotubes paste electrode modified with bismuth powder has been used for the diagnosis of *Helicobacter pylori* by using adsorptive stripping voltammetry (combined with an anodic scan) [41]. Finally, the determination of formic acid (herein, acting as an ingredient in fuel cells) was performed by cyclic voltammetry using a mesoporous Pt-electrode covered with a bismuth film [20].

Conclusions

This article demonstrates that bismuth–based electrodes can successfully be used for analysis of organic compounds. Limits of detection for toxic nitro-organic species and pesticides at bismuth electrodes are quite satisfactory (normally achieving sub-μmol L^{-1} concentration levels) but the inherent selectivity of voltammetric techniques is not sufficient for their determination in complex environmental samples. Therefore, these sensors are very useful for screening purposes.

On the contrary, azo-dyes and some pesticides are effectively detectable in food samples using bismuth electrodes and voltammetric detection. Similarly, many drugs can be electrochemically quantified directly in pharmaceuticals preparations at bismuth electrodes. Finally, bismuth–based electrodes, combined with a bio-recognition species, can be used as biosensors for the determination of biologically important molecules in clinical samples since the required selectivity is provided by the biologically specific interaction.

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