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Voltammetric behavior of $I_2/2I^-$ redox system on boron-doped diamond electrode in various media and its utilization for the indirect detection of tin(II)

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ABSTRACT

Simple and fast electroanalytical method for the detection of tin(II) in bronze has been developed. It is based on synergistic combination of boron-doped diamond electrode as sensitive voltammetric sensor and reaction electrochemistry. The voltammetric response is enhanced by chemical recycling of iodide after electrogeneration of iodine followed by reaction with Sn(II). The charge transfer for the oxidation of iodide to iodine on boron-doped diamond electrode was investigated and characterized in eight different electrolytes. Charge transfer coefficient (0.58 in 0.1 mol L^{-1} H_3PO_4–0.35 in 0.1 mol L^{-1} HCl), formal potential (0.65 V in 0.1 mol L^{-1} $HClO_4$–0.90 V in 0.1 mol L^{-1} $NaHCO_3$) and standard heterogeneous rate constant (4.6×10^{-3} cm s^{-1} for H_3PO_4–2.2×10^{-3} cm s^{-1} for $NaHCO_3$) were estimated. Based on these values it was observed that the charge transfer is irreversible, but the response is suitable for the quantification of tin(II) in bronze for tire cords. The detection limit of 2.3×10^{-7} mol L^{-1} was achieved by linear sweep voltammetry. This value is comparable with some expensive and time consuming techniques routinely used for this type of determination.

1. Introduction

Tin is widely used in various alloys like bronze, brass and in materials for soldering. It has two basic chemical forms: a strong reductant Sn(II) is more toxic than more stable Sn(IV) [1]. In this time tin and its compounds serve as a material for cans in food and beverage industry, therefore tin may be dissolved into food products and take a part in a food chain [2,3]. The maximum daily intake of tin should not exceed 2 mg kg^{-1} and maximum concentration limits of tin are 200 mg kg^{-1} for food products and 100 mg kg^{-1} for canned beverages [4,5]. Tin compounds are used also in fungicides, molluscides, ovicides, rodenticides, conservants, anticorrosive formulations and catalysts in biofuel production [6,7]. Tin is very important element in rubber industry as polybutadiene rubber stabilizer as well as compound of bronze for tire cords for obtaining tire stability on wheel disc [8].

For the detection of tin in various matrixes several kinds of analytical techniques have been used e.g. absorption spectrometry with electrothermal atomization in graphite furnace (GF-ETAAS) [9,10]. This technique with a detection limit of 1.7×10^{-7} mol L^{-1} does not distinguish various oxidation states of tin and is relatively expensive as well as flame absorption spectrometry [11] (F-AAS) with LOD of 7.1×10^{-8} mol L^{-1}. Very sensitive is ICP-OES technique (LOD = 6.8×10^{-9} mol L^{-1}) where sample is decomposed by high pressure or by microwaves in the presence of HNO_3, H_2O_2 and HCl [12]. UV–VIS spectrometry [13] (LOD = 1.5×10^{-7} mol L^{-1}) and X-Ray fluorescence [14] (LOD = 4.2×10^{-7} mol L^{-1}) are used as detectors in chromatographic systems for detection of tin. ICP method coupled with MS-ESI is a powerful detection technique in ion chromatography for the fast and simultaneous detection Sn(II) and Sn(IV) in water. It is based on complexation of both tin forms by diethylenetriaminepentaacetic acid (DTPA) and the retention of $[Sn(DTPA)]^{3-}$ and $[Sn(DTPA)]^{-}$ complexes. Linear response of this detection system in the concentration range of 8.5×10^{-9}–8.5×10^{-6} mol L^{-1} was obtained [15].

Electrochemical techniques are able to recognize various forms of tin. The most sensitive for Sn(II) has been found anodic stripping square-wave voltammetry by using bismuth film electrode in the presence of cetyltrimethylammonium bromide with a detection limit of 2.2×10^{-9} mol L^{-1}. This method was successfully applied in the analysis of canned fruit juices as well as of sea water in the presence of catechol as adsorptive complexing agent for Sn(II) [16]. This methodology was also used on mercury and glassy carbon electrode modified with multiwalled carbon nanotubes (MWCNT) and methylene blue [17]. Another approach is based on static electrochemistry [18] where equilibrium potential of Sn(II) ionselective electrode is measured. This device is based on PVC membrane and dibenzo-18-crown-6 (DB18C6) as a membrane carrier. The response was Nernstian in the range of 10^{-6}–10^{-3} mol L^{-1} in acidic media. This method is highly selective, however

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Table 1
Comparison with previous electrochemical methods and proposed method in this contribution.

Method	System/ electrode	LOD [nmol L^{-1}]	Linear range [nmol L^{-1}]	Sensitivity	RSD [%]	Ref.
SWASV	BiFE	140	170–7830	480 nA L mol^{-1} cm^{-2}	3.6	16
ASV	BiFE	2.19	8.42–842	–	7.3	17
SWASV	HMDE	0.295	–	–	4.7	18
POT	DB18C6/Sn(II)-ISE	800	1000–10,000,000	27.5 ± 0.6 mV	–	19
ASV	CUPFERRON/ MWCNTE	1.01	2.53–2100	–	1.5	20
DPV	HMDE	25.3	67.4–4210	48.40 nA L μmol^{-1}	–	21
DPP	DME	1260	4210–1,850,000	–	0.88	22
AdCSV	Sn(IV)-BHBA/ HMDE	0.04	0.084–337	–	2.7	23
AdSV	HMDE	0.19	2.1–211	–	7.8	24
CSV	NAFION/GCE	0.84	0.84–7.58	–	–	25
LSV	$I_2/2I^-$/BDDE	230	2000–12,000	39 nA L μmol^{-1}	>5	This paper

POT — potentiometry, DB18C6 — dibenzo-18-crown-6, CUPFERRON/MWCNTE — N-nitrozo-N-phenylhydroxylamine/multiwalled carbon nanotube electrode, DPP — differential pulse polarography, AdCSV — adsorptive catalytic stripping voltammetry, DHBA — 3,4-dihydroxybenzoic acid, AdSV — adsorptive stripping voltammetry, CSV — cathodic stripping voltammetry, (dash "–"means that data has not been published).

it need time for establishment of the equilibrium as well as higher errors of determination due to antilogarithmization may occur [19] (for comparison with other electrochemical methods see Table 1 [20–25]).

In this paper we would like to extend number of fast and cheap electrochemical approaches for tin detection. The method proposed here successfully utilizes combination of boron-doped diamond electrode as sensor together with reaction electrochemistry using $I_2/2I^-$ redox system.

2. Experimental

All electrochemical experiments were carried out in three electrode arrangement in a glass electrochemical cell maintained at 25.0 ± 0.5 °C. Boron-doped diamond film electrode with a diameter of 3 mm in polyetherether ketone (PEEK) tube (Windsor Scientific Ltd., UK) served as working electrode. Classical Ag/AgCl (3 mol L^{-1} KCl) electrode was used as reference and platinum electrode with area of 1 cm^2 as counter electrode. Voltammetric measurements were realized on Autolab PGSTAT 302N (Metrohm Autolab BV, Holland) potenciostat/galvanostat controlled with GPES 4.9 software. The surface of working electrode was cleaned by ultrasound (Elmasonic P, Elma Hans Schmidbauer GmbH & Co. KG, Germany), followed by polishing with alumina suspension in deionized water, and finally activated electrochemically at constant potential of +5.0 V vs. Ag/AgCl for 60 s before each measurement.

All chemicals were of p. a. purity. Deionized water (EUROWATER, Bratislava) was used for all solutions. HCl (0.1 mol L^{-1}, MIKROCHEM Pezinok), H_3PO_4 (0.1 mol L^{-1}, LACHEMA Brno), $HClO_4$ (0.1 mol L^{-1}, CENTRALCHEM Bratislava), $NaH_2PO_4 \cdot H_2O$ (pH = 4.6; 0.1 mol L^{-1}, LACHEMA Brno), acetate buffer solution with pH value of 4.7 (0.1 mol L^{-1}, prepared from 0.2 mol L^{-1} $CH_3COONa \cdot 3H_2O$ — LACHEMA Brno and 0.2 mol L^{-1} CH_3COOH — MIKROCHEM Pezinok), KCl (0.1 mol L^{-1}, LACHEMA Brno), $NaHCO_3$ with pH of 8.3 (0.1 mol L^{-1}, LACHEMA Brno) and Na_2HPO_4. $12H_2O$ with pH of 9.8 (0.1 mol L^{-1}, LACHEMA Brno) served as supporting electrolytes.

The series of the solutions with various concentrations were prepared by dilution from stock solutions prepared from solid chemicals of KI (LACHEMA Brno) and $SnCl_2.2H_2O$ (LACHEMA Brno). For the preparation of 0.01 mol L^{-1} solution of $SnCl_2$. $2H_2O$ 2.4 mol L^{-1} hydrochloric acid was used as solvent. 125 mL of supporting electrolyte was pipetted into electrochemical cell and 100 mg of solid KI was added to form 5×10^{-3} mol L^{-1} KI solution for voltammetric measurements. Calibration solutions had concentrations of 2,4,6,8,10 and 12 μmol L^{-1}. The solutions were bubbled with a pure nitrogen for 10 min before each voltammetric measurement. 300 mg of bronze for tire cord was weighed, powdered and tin was leached from the alloy by concentrated HCl at elevated temperature to be converted on Sn(II). As for selectivity of this method we investigated three metals which may be present in the samples and we observed that 100 hundred excess of iron(III) does not affect the determination, as well as manganese(II) because it is well known that in strongly acidic solutions no formation of MnO_2 is occur as a possible electrode fouler. The copper(II) strongly affects determination of Sn(II), because chemical formation of I_2 reacting with Sn(II) prior LSV registration.

Thus, HCl or diluted H_2SO_4 should be used for tin leaching to avoid copper dissolution. After filtration of insoluble copper portion the volume was filled at the mark of 500 mL volumetric flask. From this flask 12.5 mL of the sample were pipetted into 125 mL volumetric flask, 100 mg of solid KI were added then volume was filled with supporting electrolyte. This solution was transferred into electrochemical cell. Six additions of 5 μL of 0.01 mol L^{-1} $SnCl_2$ were added and multiple standard addition method was used for Sn(II) quantification.

3. Results and discussion

First, we investigated voltammetric behavior of iodide on boron-doped diamond electrode and its heterogeneous charge transfer in various media. In Fig. 1 cyclic voltammograms for various scan rates of 5×10^{-3} mol L^{-1} KI solution in eight supporting electrolytes are shown. Cyclic voltammograms were measured in a strongly acidic media ($HClO_4$, HCl, pH = 1), weakly acidic media (H_3PO_4, pH = 1.7, NaH_2PO_4, pH = 4.6, acetate buffer solution, pH = 4.7), neutral media (KCl, pH = 7) and weakly alkaline media ($NaHCO_3$, pH = 8.3, Na_2HPO_4, pH = 9.8). Nicely developed oxidation peak was observed in all electrolytes, however no reduction peak more than 500 mV from the oxidation peak. Concluding this, the charge transfer of iodide oxidation on boron-doped diamond electrode is irreversible.

In Fig. 2 is depicted the dependence of peak current on square root of scan rate. These dependencies for all electrolytes were found to be linear in the range of 25–300 mV s^{-1}. The oxidation of iodide to iodine is such controlled by diffusion and no adsorption or another surface processes take place in the charge transfer. This is consistent with the fact that boron-doped diamond surface has very low ability to be modified by chemical or physical manner. Charge transfer coefficients were calculated according to well-known criterion based on peak potential E_p and potential corresponding to half-height of peak $E_{1/2}$ expressed by this equation [26]:

$$|E_p - E_{1/2}| = \frac{47.7}{\alpha z} \text{mV at } 25\ ^\circ\text{C} \quad (1)$$