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Possibilities and limitations of the determination of zinc(II) at gallium film electrodes. An initial study

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In this paper, basic electroanalytical properties and behaviour of the gallium film-plated electrodes (GaFEs) are presented. Being prepared by electrodeposition and plating onto two different carbonaceous electrode substrates, the following experimental characterisation of the individual GaFEs has been focused on their possible employment in stripping voltammetry. The most satisfying performance and fairly low background currents were achieved in acetate buffer or diluted hydrochloric acid, when using the square-wave voltammetric mode. The electroanalytical performance of a method with GaFE has been tested on model determinations of Zn(II) ions with satisfactory results.

Key words: gallium film(s), glassy carbon- and carbon paste electrode substrates, anodic stripping voltammetry, zinc, determination

INTRODUCTION

Electrochemical stripping analysis has been widely recognized as a powerful and highly sensitive technique for the determination of trace metals [1]. For lengthy decades, the hanging mercury drop electrode (HMDE) and mercury film electrodes (MFEs) have been used as the working electrodes of choice; however, the controversial character of liquid mercury and, mainly, high toxicity of its compounds have become inacceptable for ecologically oriented analysts, popularising the concept of *green chemistry* – one of the leading trends in chemical sciences since the commencement of the new millennium [2].

Wang's research group [3] was one of the first groups who had reflected the changed reality and offered the full-value alternative to the MFE – a bismuth film (coated) electrode, BiFE, that soon initiated the real boom in the field [4–6], establishing also a brand new area of electroanalysis with the so-called non-mercury metallic film electrodes [6]. This rapidly growing family comprises (i) a wide variety of BiFEs [6] and related arrangements, including bismuth bulk electrode (BiBE [7]), bismuth powder- or bismuth trioxide-modified carbon paste electrodes (Bi-CPE [8] and Bi_2O_3-CPE [9], respectively), (ii) antimony film electrodes (SbFEs [10, 11]), plus some (iii) other configurations, such as PbFEs [12], SnFEs [13], or even a SeFE [14], representing so far the only known example of semimetal film-based electrode.

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Concerning the gallium film electrode, GaFE, there are a few reports [15–17], mostly having utilised the well-known effect of trivalent Ga(III) in suppressing the interferences from Cu(II) ions [18–20]. (Gallium itself belongs among less frequent toxic metals – together with indium – whose environmental impact is now of considerable interest due to their increasing use in semiconductors and LED technologies [2]).

In this report, attention is paid to functioning of gallium in the metal film arrangement; namely, as gallium film plated glassy carbon- and carbon paste electrodes (GaF-GCE and GaF-CPE, respectively) The behaviour of both types of electrodes has been studied and evaluated in terms of specific electrodeposition in the pure form and as gallium alloys, as well as of potential applicability in stripping voltammetry, offering yet another alternative to the above-mentioned metal film configurations.

EXPERIMENTAL

Chemicals and reagents

All chemicals used were of analytical reagent grade and purchased from Sigma-Aldrich or Merck unless stated otherwise. Two main stock solutions of acetate buffer (AcB; equimolar mixture of $CH_3COOH + CH_3COONa$) and hydrochloric acid were made 1 M in concentration. Other solutions, including some complex-forming media, were $HClO_4$, NaOH, ammonia and phosphate buffers (0.5 M), KCl, KBr and citrate (0.1 M), plus EDTA (0.01 M). Stock solution of Ga(III) used for the in-situ generation of the respective films was prepared from solid $Ga(NO_3)_3$. Finally, stock standard solutions of three model ions, Zn(II), Cd(II), and Pb(II), were prepared as 1.0 mg L^{-1} (from commercial AAS standards) and acidified to pH 2. All solutions were made from deionised water (Elix 10/Milli-Q Gradient unit, Millipore, Bedford, USA).

Apparatus and instrumentation

All the measurements were performed with an AUTOLAB electrochemical analyser (model PGSTAT 30; Ecochemie, Utrecht, Holland) operated by means of NOVA 1.6 software (the same manufacturer). A three-electrode cell used comprised the working electrode (see below), a Ag/AgCl/3M KCl as the reference (further abbreviated as "ref."), and a Pt-plate as the auxiliary electrode. For more effective deposition, the stirring was devised with a Teflon®-coated magnetic bar rotated at ca. 300 rpm.

Working electrodes

Glassy Carbon Electrode. For measurements, the glassy carbon electrode (GCE) with the surface diameter of 2 mm was used and each new week polished with 0.05 µm alumina powder (Micropolish II, Buehler, USA) using a polishing pad (Microcloth, Buehler, USA).

Carbon Paste Electrode. The carbon paste mixture was prepared by thoroughly hand-mixing 1.0 g of spectroscopic graphite powder (CR-5 type; Maziva Týn, Czech Republic) with 0.6 mL of highly viscous silicone oil (LUKOIL MV 8000; Lučební závody Kolín, Czech Republic). Both components were homogenized using the recommended procedure [21] and roughly equal portions of the freshly made carbon paste packed into the identical piston-driven holders of our own design [22]. Each electrode prepared had been checked on its ohmic resistance and values below 10 ohms indicated good homogeneity [21].

Procedures

Preparation of working electrodes for measurements. Gallium films were deposited in situ, i. e. by potentiostatic electrolysis performed directly in sample solutions with Ga(III) ions. The carbon paste surface was renewed mechanically by its smoothing with wet filter paper [21] and this operation was usually made prior to each new set of measurements. The glassy carbon surface was renewed by electrochemical cleaning / conditioning at +0.3 V vs ref. for 5 min and, if needed, polishing the glassy carbon surface with 0.05 µm alumina powder.

Square-Wave Anodic Stripping Voltammetry (SWASV). Typical experiments comprised a pre-concentration step at −1.50 V vs ref., followed by a 15 s equilibration period and the anodic scanning from −1.50 V up to 0.0 V. The SWV-modulation ramp was set as follows: pulse amplitude, ΔE_{SW} = +50 mV; frequency, f_{SW} = 25 kHz; the potential increment, i_{SW} = 5 mV. Some parameters could slightly be varied and, therefore, the actual values are always specified in the legend of each figure presented.

RESULTS AND DISCUSSION

Gallium film formation at the glassy carbon and carbon paste electrodes

A set of preliminary experiments had already indicated that the gallium film could be deposited in situ onto a suitable carbonaceous substrate electrode, which also confirmed some previous results [17]. The corresponding assay has been carried out with two different carbon substrates, GCE and CPE, in a solution of 0.1 M acetate buffer taken as the model supporting electrolyte and with two different concentrations of 5 and 10 mg L^{-1} Ga(III). Due to a highly negative potential required for dissolution of gallium and according to some previous experiences [17,23], the deposition had always been performed at potentials more negative than −1.5 V vs Ag/AgCl. Only in this way, it was possible to define the full operational range ("potential window") of the respective GaFE available between the hydrogen evolution (upper limit, beyond −1.5 V) and the dissolution peak itself (lower limit, about −1.0 V vs ref.)

The proper dissolution process, i. e. reoxidation $Ga^0 \rightarrow Ga^{III}$, is shown in Figs. 1 and 2, making comparison of the performance of two different GaFEs operated in situ and prepared from two different substrates under the same conditions. All voltammograms confirm the functionality of

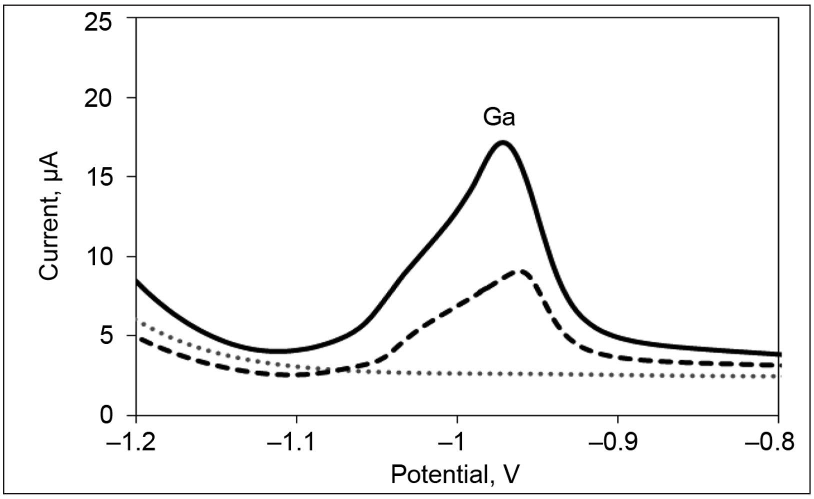

Fig. 1. Square-wave voltammograms of $Ga^0 \longrightarrow Ga^{III}$ reoxidation at the glassy carbon substrate. Blank (dotted line), 5 mg L^{-1} Ga(III) (dashed line), 10 mg L^{-1} Ga(III) (solid line). Experimental conditions: deposition, $E_{DEP} = -1.7$ V vs ref., $t_{DEP} = 60$ s. Supporting electrolyte 0.1 M acetate buffer (pH = 4.5)

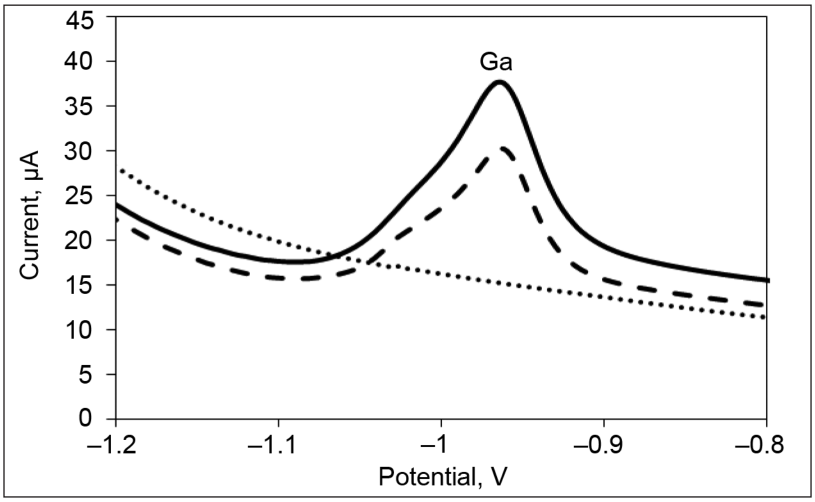

Fig. 2. Square-wave voltammograms of $Ga^0 \longrightarrow Ga^{III}$ reoxidation at the carbon paste substrate. Blank (dotted line), 5 mg L^{-1} Ga(III) (dashed line), 10 mg L^{-1} Ga(III) (solid line). For other conditions, see Fig. 1 and Experimental part

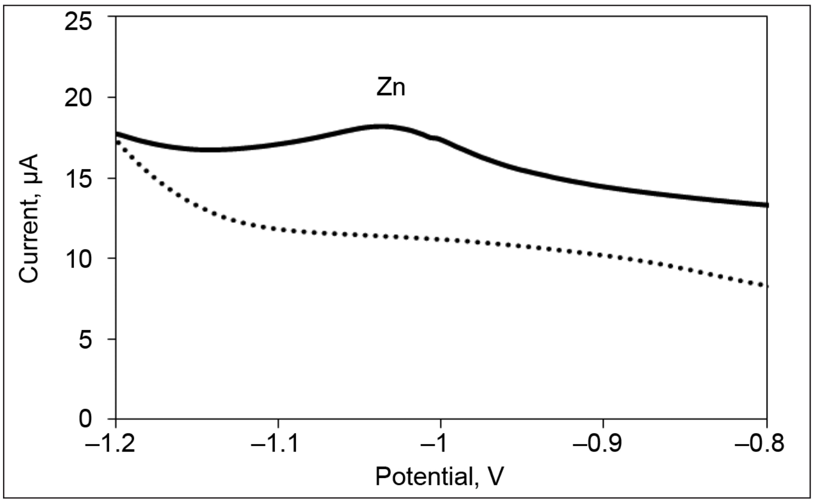

Fig. 3. Square-wave voltammograms of Zn(II) at the carbon paste substrate. Blank (dotted line), 60 µg L^{-1} Zn(II) (solid line). For other conditions, see Fig. 1 and Experimental part

both film electrodes, as well as somewhat better developed response of the GaF-CPE configuration, indicating somewhat better behaviour of the deposited film at the carbon paste-based substrate.

Anodic stripping voltammetry of Zn(II)
In anodic stripping voltammetry with common non-mercury electrodes, the determination of Zn(II) is less reliable compared to those applicable to Pb(II), Cd(II), or Cu(II). At first, there is lesser efficiency of the zinc deposition [23] inevitably reflected in limited detection capabilities (for higher concentration levels) and, second, the reduced zinc readily forms various intermetallic compounds, especially with Cu(II), that may seriously interfere in its determination [23].

The possible detection of Zn(II) at the bare GCE and CPE was investigated next, confirming fully the above-mentioned less effective deposition and limited detection capabilities as one can see on the resultant voltammograms in Fig. 3. Interestingly, the signal at the GCE had been split into two small signals of unknown nature. The overall response was again worse compared to that obtained with the CPE, therefore the carbon paste-based substrate was selected for further studies.

SWASV of zinc(II) at the GaF-CPE in acetate buffer

The already discussed specific effect of Ga(III) to suppress the interferences between zinc and some other metals, especially copper [18–20], was behind an idea to utilize similar principles also for the determination of Zn(II) with the gallium film configuration, herein with GaF-CPE. The respective test was made with GaFE operated in situ, when the concentrations of both Ga(III) and Zn(II) were similar to those in two previous experiments. All the measurements had been made in 0.1 M acetate buffer under the same conditions and with already set parameters.

The result is depicted in Fig. 4, revealing that even rather narrow potential range of the GaF-CPE would enable to indicate the response of zinc, appearing as a sharp signal (with E_p of about –1.05 V vs ref.) at the left foot of the dissolution peak of gallium. Whereas the Figure shows

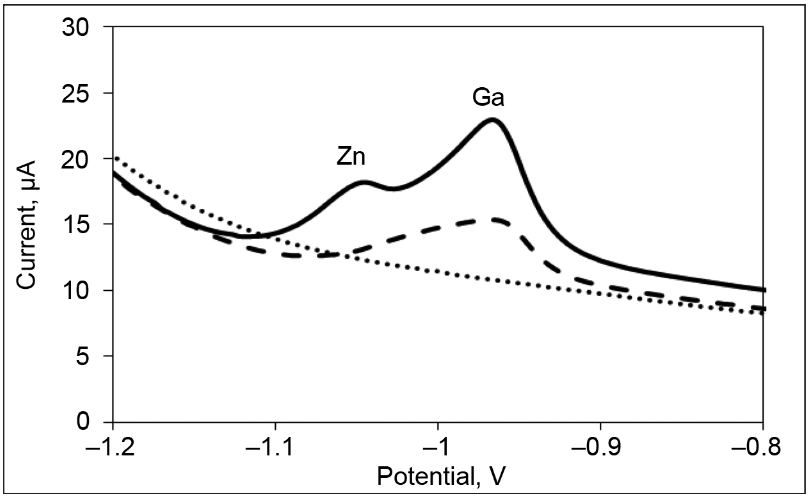

Fig. 4. Square-wave voltammograms of Zn(II) at the gallium film plated carbon paste electrode, GaF-CPE. Blank (dotted line), 5 mg L^{-1} Ga(III) (dashed line), 5 mg L^{-1} Ga(III) and 50 µg L^{-1} Zn(II) (solid line). For other conditions, see Fig. 1 and Experimental part

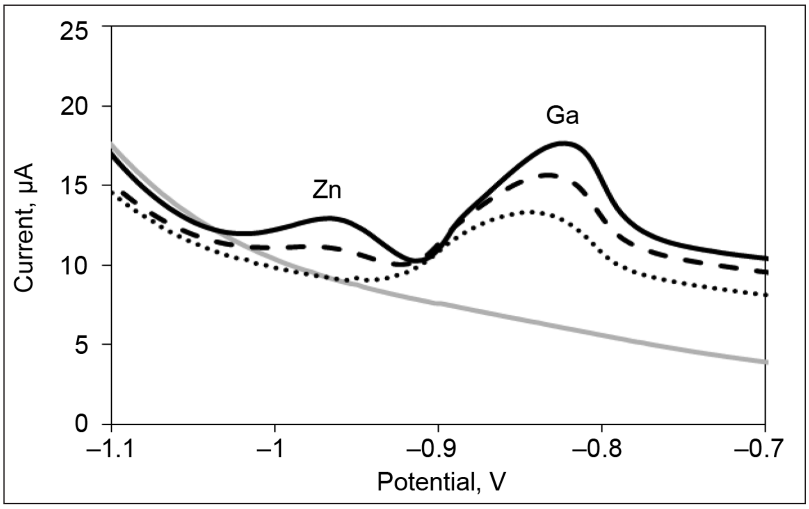

Fig. 5. SWASV of Zn(II) at the GaF-CPE in 0.01 M HCl. Blank (grey line), 5 mg L^{-1} Ga(III) (dotted line), 5 mg L^{-1} Ga(III) and 50 µg L^{-1} Zn(II) (dashed line), 5 mg L^{-1} Ga(III) and 100 µg L^{-1} Zn(II) (solid line). For other conditions, see Fig. 1 and Experimental part

the particular experiment with one model concentration, the subsequent calibrations have resulted in finding that zinc could be detected within a concentration interval of ca. 10–50 µg L^{-1} Zn(II). Whereas the concentrations lower than 10 µg L^{-1} Zn(II) could not be detected due to the insufficient sensitivity (see the commentary above), the concentrations above 50 µg L^{-1} Zn(II) were unachievable as well, due to the close position of both Zn- and Ga- reoxidation signals and their undesirable overlaps.

SWASV of zinc(II) at the GaF-CPE in other supporting media

To investigate nuances in the simultaneous deposition of zinc and gallium and their consequent reoxidation during the stripping step, a series of different supporting electrolytes was tested, namely: 0.1 M ammonia buffer (pH = 9), 0.1 M phosphate buffer (pH = 7.5), 0.01 M HCl, 0.01 M $HClO_4$ (both pH ca. 2), and 0.1 M NaOH (pH ca. 13); some of these solutions with additions of 0.01 M KCl, KBr, and citrate or even 0.001 M EDTA.

In fact, compared to 0.1 M acetate buffer and its use as a model medium (described above), none of newly tested solutions led to any significant improvement of both peaks of interest and their mutual resolution, perhaps except diluted hydrochloric acid for which the respective voltammograms are shown in Fig. 5. It is worth to note that the linear dependence of current on Zn(II) concentration was observed in the range from 10 to 50 µg L^{-1}, whereas in the case of higher Zn(II) concentrations the deviations were found.

The set depicted documents a fine and smooth blank and, in two subsequent scans, a fairly proportional increase of the signal for zinc (with $E_p = -1.0$ V vs ref.), whereas the magnitude of the (large) dissolution peak of gallium has remained practically unchanged. One can notice its certain shift to the less negative potentials, which is a phenomenon typical for metal film electrodes and higher concentrations of the reoxidised species [23, 24].

CONCLUSIONS

It has been shown that the gallium film plated in situ and preferably onto the carbon paste-based support can be employed as a detection tool in anodic stripping voltammetry of Zn(II) at the trace concentration level (in an interval of 10–50 µM Zn(II)). Otherwise, the study described was of the initial character and performed solely with model solutions.

Undoubtedly, the method presented requires to be further elaborated, especially in terms of prevention of possible interferences from other metal ions and, in general, all the species occurring in typical real samples.

In prospect, the GaF-CPE configuration is potentially applicable also to other metal ions with more negative reoxidation potentials, such as Ni(II) and Co(II) or Mn(II), which would be, in itself, beneficial in electroanalysis with non-mercury metal film-based electrodes [25].

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Zn(II) NUSTATYMO GALIMYBĖS IR APRIBOJIMAI NAUDOJANT GALIO PLĖVELINIUS ELEKTRODUS. PRADINĖ STUDIJA

Santrauka

Skirtingose buferinėse sistemose tirti galio plėvelinio elektrodo formavimo *in situ* būdu ypatumai. Ištirtas galio plėvelinio elektrodo panaudojimas Zn(II) koncentracijos nustatymui modeliniuose tirpaluose. Galio plėvelės buvo nusodinamos ant stikliškosios anglies ir anglies pastos elektrodų. Geriausi rezultatai esant žemoms foninėms srovėms gauti atliekant kvadratinės bangos voltamperometrijos tyrimus 0,1 M acetatiniame buferyje (pH = 4,5) ir praskiestame 0,01 M druskos rūgšties tirpale, galio plėvelės nusodinimui naudojant anglies pastos elektrodą. Gauti rezultatai parodė, kad galio plėvelės nusodintos *in situ* būdu ant anglies pastos elektrodo gali būti naudojamos anodinėje inversinėje voltamperometrijoje Zn(II) nustatant koncentracijas 10–50 µg L^{-1} ribose.