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ORIGINAL PAPER

Study on simultaneous measurements of trace gallium(III) and germanium(IV) by adsorptive stripping voltammetry using mercury film electrode

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Abstract Simultaneous adsorptive stripping voltammetric method for the determination of trace gallium(III) and germanium(IV) based on the adsorption of gallium(III) and germanium(IV)-catechol complex on the cyclic renewable mercury film silver based electrode (Hg(Ag)FE) is presented. The calibration graph is linear from 1.25 nM (0.09 μg L^{-1}) to 90 nM (6.27 μg L^{-1}) with correlation coefficient of 0.999 for gallium and from 2.5 nM (0.18 μg L^{-1}) to 160 nM (12.3 μg L^{-1}) with correlation coefficient of 0.998 for germanium for a preconcentration time of 30 s. The detection limit for a preconcentration time of 60 s is as low as 25 ng L^{-1} for gallium and 58 ng L^{-1} for germanium. The proposed method was successfully applied by studying the natural samples and simultaneous recovery of Ga(III) and Ge(IV) from spiked water and sediment samples.

Keywords Gallium · Germanium · Catechol · Trace analysis · Mercury film electrodes · Adsorptive stripping voltammetry

1 Introduction

Gallium is considered one of the rare elements. The interest in the determination of gallium traces in the environment or in biological samples is increasing in consideration of the technological or biological applications of this element. The large use of gallium arsenide in the semiconductor industry produces its mobilization and diffusion. Due to the latter application, the world production is increasing and level of gallium in the environment is beginning to rise, mainly around industrial areas [1, 2]. Gallium is not known to be essential in biological systems and so far is not considered toxic.

Few analytical techniques possess the sensitivity required for trace and ultratrace quantitation of gallium [3]. The most widely used techniques for the determination of gallium are atomic absorption spectrometry (AAS) [3–5], neutron activation analysis [6–9], and atomic emission spectrometry [10]. The utility of neutron activation methods, which permit measurements down to ultratrace level, is restricted by instrumentation cost, long exposure times, or matrix interference [3]. With spectrometry techniques, such as atomic or molecular absorption or fluorescence, detection limits are substantially higher [3]. Inductively coupled plasma mass spectrometry [11] has been described for gallium determination, but it requires expensive instrumentation, which is not available to most laboratories. Many electroanalytical procedures have been proposed for the determination of trace amounts of gallium. Using single-sweep polarography, Ga(III) can be measured in the presence of organic ligands, such as bromopyrogallol red [12] and alizarin violet [13]. The conventional anodic stripping determination of gallium is based on the formation of its amalgam. The best results were achieved in solutions containing thiocyanate or salicylic acid [14–17]. However, because of the negative peak potential of gallium, its stripping response is masked by the hydrogen evolution current when acidic solutions are used. And the accuracy of the measurement is adversely affected by the formation of intermetallic compounds between gallium, zinc, copper, and nickel. It has been shown that trace and ultratrace quantities of gallium can be determined by

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means of adsorptive stripping voltammetry using salicyl fluorone [18], solochrome violet RS [19], ammonium pyrrolidine dithiocarbamate, pyrocatechol violet, and diethyldithiocarbamate [20].

Germanium is an important trace element in the human body. Both accumulation and deficiency of germanium result in various diseases. Accumulation of germanium in the tissues can lead to acute renal failure [21] and, on the other hand, deficiency of germanium to tumour formation and cancer [22, 23]. For human beings, trace germanium in the body is taken from the air, water, and especially from food. Accordingly, the determination of germanium is very important.

Several analytical methods exist for the determination of germanium, including flame atomic absorption spectrometry (FAAS) [24] and graphite furnace atomic absorption spectrometry (GFAAS) [25], inductively coupled plasma atomic emission spectrometry (ICP-AES) [26], and UV spectrophotometry [27]. The determination of germanium by AAS can suffer from high detection limits and poor reproducibilities. To improve the detection limits, one must use hydride generation when using FAAS. On the other hand, the GFAAS technique is faced with the volatilization of GeO formed before the atomization step, just as with ICP spectrometry. UV methods require very specific reagents and are rarely free of interferences, especially in cases where the germanium concentration in the sample is very low. Electroanalytical methods are useful tools in the analysis of traces germanium. Germanium(IV) complex with organic ligands such as polyhydroksy compounds [28–31] have been applied in the polarographic determination of germanium, but these methods are not sufficiently sensitive to detect trace germanium. The sensitive adsorptive stripping measurements of germanium(IV) in the presence of catechol and pyrogallol have been reported [32, 33], and the method has been applied to determination of trace germanium in ginseng, garlic and ore samples.

Most voltammetric methods required mercury electrodes. The *HMDE* is the electrode of preference due to its high sensitivity, reproducibility, and linearity. However, the toxicity of mercury limits the usage of the mercury electrodes in the analytical practice and excludes them from the out-of-laboratory applications. The problem of limiting the amount of mercury or its soluble salts needed for the analytical procedure can be solved with the help of a renewable silver amalgam film electrode. The principle of working and first proposal of a construction of the Hg(Ag)FE was described in [34]. Next, the construction of the electrode has been developed and described in [35]. The simple construction of the applied electrode allows the mercury film to be refreshed before each measurement. The procedure of refreshing the outer mercury film involves two steps: pulling up the silver electrode base inside the electrode body, through the mercury chamber, and then pushing it back outside the electrode body. During these movements, the silver wire base comes into contact with the liquid mercury twice. The total volume of the liquid mercury used to fill up the chamber does not exceed 10 μL. Usually after 2000 cycles, the whole mercury/mercury silver amalgam from the chamber of Hg(Ag)FE is replaced. The Hg(Ag)FE refreshed before each measurement demonstrates many properties which are specific only to the hanging mercury electrode. On the other hand, comparing to the later, Hg(Ag)FE is characterized by mechanical durability and wide range of surface regulation. The repeatability of the electrode is 1–2%, and the reproducibility of the electrode is several per cent.

The Hg(Ag)FE electrode was successfully applied for the determination of Pb, Zn, Cd, Cu, Cr, Co, Ni, elemental S, Mn, Mo, Se, U, Pd, Ga, Sc [34–45].

Other recent mercury film electrodes in the determination of trace beryllium at the mercury film electrode [46], trace vanadium at the mercury-coated micro-wire and polystyrene-coated bismuth film electrodes [47], and oxcarbazepine at the silver nanoparticle-modified carbon screen-printed electrodes in stripping voltammetry were applied [48].

In this study, differential pulse adsorptive stripping voltammetry (*DPAdSV*) is applied for the trace gallium(III) and germanium(IV) determination in the presence of catechol as a complexing agent. The new procedure was examined and successfully utilized for simultaneous fast determination of low and high gallium(III) and germanium(IV) concentration in a natural water and sediment samples. Potential interference from selected metal ions and surface-active substances were checked.

2 Experimental

2.1 Measuring apparatus and software

A multipurpose Electrochemical Analyzer M161 with the electrode stand M164 (both MTM-ANKO, Poland) were used for all voltammetric measurements. The classical three-electrode quartz cell, volume 20 mL, consisting of a homemade cylindrical silver-based mercury film electrode Hg(Ag)FE [34, 35], refreshed before each measurement and with a surface area of 1–12 mm^2, as the working electrode, a double junction reference electrode Ag/AgCl/KCl (3 M) with replaceable outer junction (3 M KCl), and a platinum wire as an auxiliary electrode. pH measurements were performed with laboratory pH-meter. Liquid samples were mineralized using a UV-digester (Mineral, Poland). Solid material was digested with a Uniclever II microwave digestion system (Plazmatronika, Poland).

Stirring was performed using a magnetic bar rotating at ~500 rpm. All experiments were carried out at room temperature.

2.2 Chemicals and glassware

All reagents used were of analytical grade. CH_3COOH and CH_3COONa were purchased from Merck, Suprapur®, and mercury GR for polarography from Merck. 0.01-M standard stock solutions of gallium(III) and germanium(IV) were prepared by dissolving Ga_2O_3 (Merck) in HCl (Merck, Suprapur®) and GeO_2 (Johnson, Matthey & CO., Limited, England) in NaOH (POCh, Poland). Solutions with lower gallium and germanium concentrations were made weekly by appropriate dilution of the stock solution. A fresh 0.1-M solution of catechol (Aldrich) was prepared every 2 weeks by dissolving catechol in water. Triton X-100 was purchased from Windsor Laboratories Ltd, UK, and humic acid (sodium salt) was from Aldrich. A 0.1% solution of humic acid was prepared by dissolving the primary (original) reagent in water distilled from quartz with addition of 10 μL of 10% NH_3. The silver base for the film electrode was prepared from polycrystalline silver wire with a diameter of 0.5 mm and of 99.99% purity (Goodfellow Science Park, England). Prior to use, glassware was cleaned by immersion in a 1:1 aqueous solution of HNO_3 (65%), followed by copious rinsing in distilled water.

2.3 Standard procedure of measurements

Quantitative measurements were performed using *DPAdSV* and the standard addition procedure. The procedure of refreshing the mercury film Hg(Ag)FE electrode was carried out before each measurement. A potential of −1.3 V was applied to condition the electrode after the refreshing step. The Hg(Ag)FE electrode conditioned in this way was used to determine gallium(III) and germanium(IV) in the supporting electrolyte: 0.1-M acetate buffer (pH 4.8) and 0.75-mM catechol (total volume 10 mL) contained in a quartz voltammetric cell. The potential of the electrode was changed in the following sequence: conditioning potential −1.3 V for 5 s, accumulation potential $E_{acc} = 0.10$ V for $t_{acc} = 30$ s and starting potential −0.350 V for 2 s. During the accumulation step, gallium(III) and germanium(IV) were adsorbed while the solution was being stirred (ca. 500 rpm) using a magnetic stirring bar. Then, after a rest period of 5 s, a differential pulse voltammogram was recorded in the cathodic direction from −0.350 to −1.3 V. The other experimental parameters were as follows: step potential, 2 mV; pulse potential, 75 mV; time step potential, 20 ms (10 ms waiting + 10 ms probing time). The measurements were carried out from deaerated solutions.

2.4 Sample preparation

2.4.1 Water

For *DPAdSV* determination of Ga(III) and Ge(IV) in river water samples, 40 mL of the sample was transferred directly into a quartz tube. For each sample, 20 μL of HNO_3 (65%) was added. Acidified water samples were digested by UV irradiation for 2 h.

2.4.2 Soil

For *DPAdSV* Ga(III) and Ge(IV) determination in the soil, about 250 mg of dried sample was weighed and transferred into a high pressure Teflon container and treated with 4 mL of nitric acid (65%) and 2 mL of perchloric acid (70%). The vessel was then placed into a microwave oven. Digestion of the samples was carried out with the following program: 20 min under microwave irradiation, 10 min cooling time, 5 min waiting time. Digested samples were placed on a heated plate in order to evaporate. The sample solutions were cooled to room temperature, transferred quantitatively into volumetric flasks (10 mL), and filled up to the mark with four times distilled water.

3 Results and discussion

3.1 Influence of DPV parameters on technique on gallium(III) and germanium(IV) peaks

The important parameters of the *DPV* technique are pulse amplitude (ΔE), potential step amplitude (E_s), waiting time (t_w), and sampling time (t_p). Consequently, these parameters were investigated. To optimize the conditions for gallium and germanium measurements, the following instrumental parameters were systematically varied: ΔE in the range 5–100 mV (both positive and negative mode), E_s in the range 1–6 mV, t_w and t_p from 5 to 40 ms.

For a pulse amplitude of 5 mV, the gallium(III) peak current (20 nM) was equal to 0.09 μA and the germanium(IV) peak current (40 nM) was equal to 0.2 μA and increased with increasing pulse amplitude. The best results were obtained for an amplitude of 75 mV [the peak current was ~1.6 μA for Ga(III) and ~1.4 μA for Ge(IV)]. Higher pulse amplitude (>75 mV) caused decrease of the germanium signal and increase of the gallium signal. For negative pulse amplitude, peak currents were similar. The increase in pulse amplitude from 5 to 100 mV caused the peak potential to shift from −988 to −1036 mV for Ga(III) and from −762 to −800 mV for Ge(IV), respectively. For further work, the pulse amplitude of 75 mV was applied.

Changes of the step potential have practically no influence on peak currents. The step potential of 2 mV was applied in further work.

The waiting time and probing time were changed in the range from 10 to 40 ms. The best results were obtained for waiting time and probing time of 10 ms, and this was the value chosen for further work.

3.2 Influence of catechol concentration on gallium(III) and germanium(IV) peaks

Simultaneous determination of gallium and germanium by *AdSV* method involves the presence of organic ligand. In the study, catechol was used as a complexing agent for gallium and germanium determinations. The measurements with normal pulse voltammetry indicates that Ga(III) and Ge(IV) are adsorbed on the surface of Hg(Ag)FE electrode. The gallium and germanium peak currents and their potentials depend on the concentration of catechol (Fig. 1). The addition of catechol to the base electrolyte (acetate buffer pH 4.8) is accompanied by increase of the Ga(III) and Ge(IV) peaks. For 0 mM of catechol, no Ga(III) and Ge(IV) peaks were observed. But for 0.05 mM of catechol, the Ga(III) peak current was 0.95 μA and the Ge(IV) peak current was 0.5 μA. The optimal concentration of catechol for simultaneous determination of gallium and germanium is in the range from 0.5 to 1 mM [with the peak current reaching values about 1.7 μA for Ga(III) and 1.4 μA for Ge(IV)]. Higher concentrations of catechol than 1 mM cause major decrease in the germanium peak current and increase in the gallium peak current (e.g., for 2 mM of catechol the gallium peak current was 1.9 μA and the germanium peak current was 0.5 μA). The concentration of catechol also had an influence on the peak potentials, which changed to more negative values for higher catechol concentrations, e.g., for 50 μM of catechol the gallium peak potential was −986 mV and for 3 mM of catechol the peak potential was −1070 mV. In the case of germanium for 50 μM of catechol, the peak potential was −780 mV and, for 3 mM of catechol, the peak potential was −816 mV. For further work, a concentration of 0.75 mM was used (the peak potential for gallium was −1030 mV, the peak half width was 72 mV, and the peak potential for germanium was −796 mV, the peak half width was 70 mV). The obtained precision ($n = 5$) for 10 nM of Ga(III) was 4.1% and for 20 nM of Ge(IV) was 3.7%.

3.3 Influence of preconcentration potential and time on gallium(III) and germanium(IV) peaks

Influence of preconcentration potential and time are always important factors on the sensitivity and the detection limit of the method. Optimal preconcentration potential for

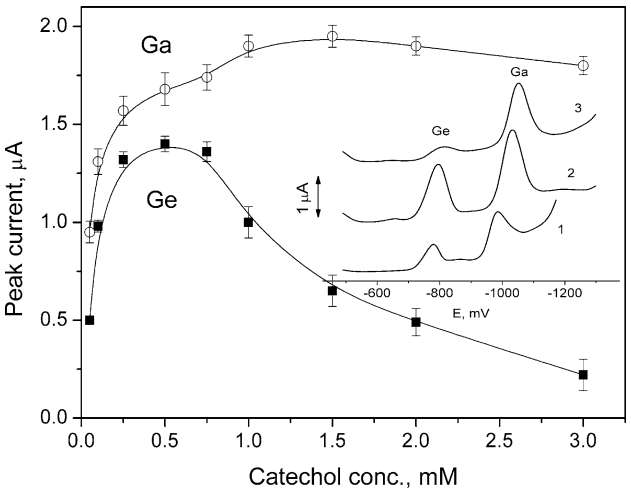

Fig. 1 Dependence of the peak currents on catechol concentration in the range from 0.05 to 3 mM for 20-nM gallium(III) and 40-nM germanium(IV) in 0.1-M acetate buffer (pH of base electrolyte 4.8) and obtained voltammogrms for *1* 0.05 mM, *2* 0.75 mM, *3* 3 mM of catechol. The electrode area was 7.7 mm^2. Instrumental parameters: $\Delta E = 75$ mV, $E_s = 2$ mV, t_w, $t_p = 10$ ms. Preconcentration potential $E_{acc} = 100$ mV and time $t_{acc} = 30$ s. Stirring rate, 500 rpm

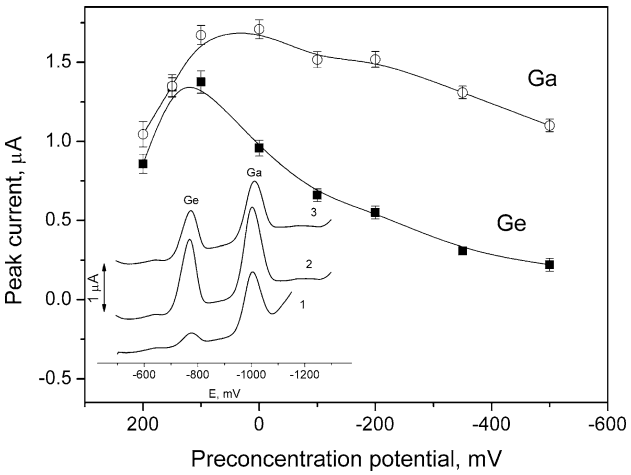

Fig. 2 Dependence of the peak currents on preconcentration potential in the range from −500 to 200 mV for 20-nM gallium(III) and 40-nM germanium(IV) in 0.75-mM catechol and 0.1-M acetate buffer (pH of base electrolyte 4.8) and obtained voltammograms for preconcentration potential of *1* −500 mV, *2* 100 mV, *3* 200 mV. All other conditions as in Fig. 1

simultaneous gallium(III) and germanium(IV) determinations in acetate buffer with catechol (pH of base electrolyte 4.8) is for 100 mV (Fig. 2). For preconcentration potentials lower and higher than 100 mV, the gallium and germanium peaks decreased significantly [e.g., for preconcentration potential of 200 mV the Ga(III) peak current was 1 μA and the Ge(IV) peak current was 0.85 μA, and for preconcentration potential of −500 mV the Ga(III) peak current was 1.1 μA and Ge(IV) peak current was 0.2 μA]. The

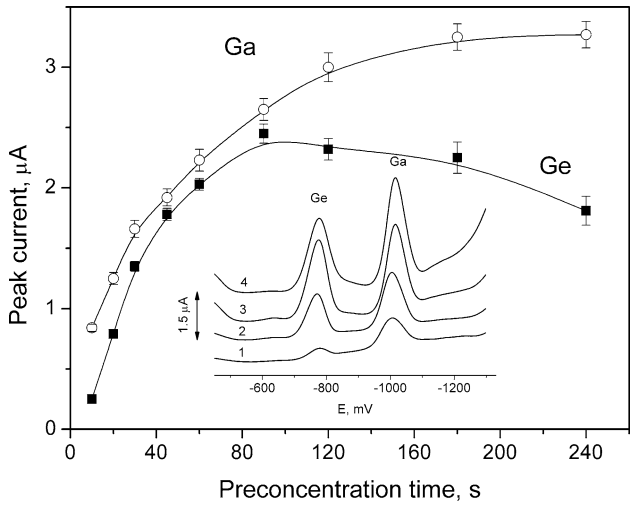

Fig. 3 Dependence of the peak currents on preconcentration time in the range from 5 to 240 s for 20-nM gallium(III) and 40-nM germanium(IV) in 0.75-mM catechol and 0.1-M acetate buffer (pH of base electrolyte 4.8) and obtained voltammograms for preconcentration time of *1* 10 s, *2* 30 s, *3* 90 s, *4* 240 s. All other conditions as in Fig. 1

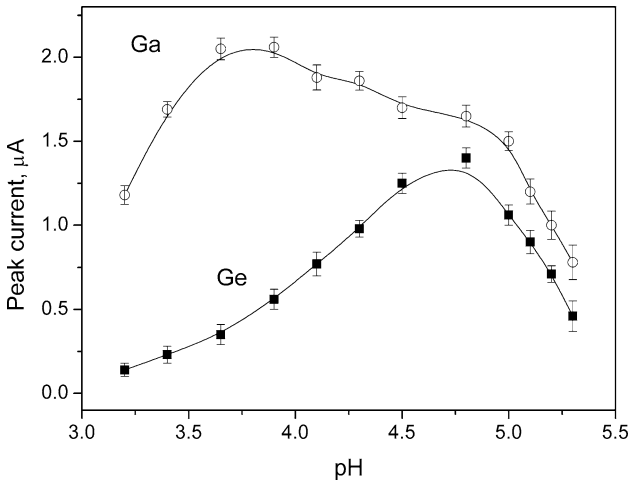

Fig. 4 Dependence of the peak currents on pH in the range from 3.2 to 5.3 for 20-nM gallium(III) and 40-nM germanium(IV) in 0.75-mM catechol and acetate buffer. All other conditions as in Fig. 1

preconcentration potential practically has no influence on the peak potentials of Ga(III) and Ge(IV). For further work, a 100 mV preconcentration potential was applied.

The changes in magnitude of the gallium and germanium currents versus preconcentration time are presented in Fig. 3. The peak currents increased with the increase of the preconcentration time, for gallium from 0.85 μA ($t_{acc} = 10$ s) to 3.25 μA ($t_{acc} = 180$ s), for germanium from 0.25 μA ($t_{acc} = 10$ s) to 2.45 μA ($t_{acc} = 90$ s). For a preconcentration time higher than 180 s, no increase of the gallium peak current was observed. For a preconcentration time higher than 90 s, the germanium peak current decreased. The gallium and germanium peak potentials are independent on the preconcentration potential and for the preconcentration time only the gallium peak potential was shifted [from −1006 mV ($t_{acc} = 10$ s) to −1016 mV ($t_{acc} = 180$ s)].

3.4 Influence of pH on gallium(III) and germanium(IV) peaks

Determination of gallium and germanium in the presence of catechol requires a medium pH to obtain a complex, which is adsorbed on the working electrode during the preconcentration step. The peak currents of Ga(III) and Ge(IV)-complex depends on the pH. In Fig. 4, the dependence of peak currents on pH is presented. The optimal pH for simultaneous determination Ga(III) and Ge(IV) was in the range from 4.5 to 4.8 (with the peak current reaching values about 1.7 μA for Ga(III) and about 1.4 μA for Ge(IV)). More acidic and more alkaline conditions caused major decrease in the germanium peak current (for the pH of 3.2 the observed Ge(IV) peak current was 0.15 μA and increased with more alkaline conditions, optimal for the pH of 4.8, next decreased, e.g., for the pH of 5.3 the Ge(IV) peak current was 0.45 μA). In the case of Ga(III) for the pH of 3.2, the observed peak current was 1.2 μA and increased with more alkaline conditions to the pH of 3.9, next decreased, e.g., for the pH of 5.3 the Ga(III) peak current was 0.8 μA. The pH also had an influence on the peak potentials, which changed to positive values for lower pH values. For example, for a pH of 5.3, the peak potentials of Ga(III) and Ge(IV) were −1070 and −846 mV and for a pH of 3.2 the peak potentials were −940 and −702 mV, respectively. For further measurements, a pH of 4.8 was applied.

3.5 Influence of the surface of the Hg(Ag)FE electrode on gallium(III) and germanium(IV) peaks

The surfaces of solid electrodes are usually much larger than those of mercury drop electrodes. When using the Hg(Ag)FE electrode, the surface of the working electrode may be varied in a wide range. The gallium and germanium peaks grew linearly as the surface of the working electrode increased in size (Fig. 5). For a surface area of 1.7 mm^2, the gallium peak current (20 nM) was 0.27 μA and grew linearly as the surface of the working electrode increased in size. For a surface area of 9.7 mm^2, the peak current was 2.11 μA. In the case of 40-nM germanium for a surface area of 1.7 mm^2, the peak current was 0.18 μA and grew linearly as the surface of the working electrode increased in size. For a surface area of 9.7 mm^2, the peak current was

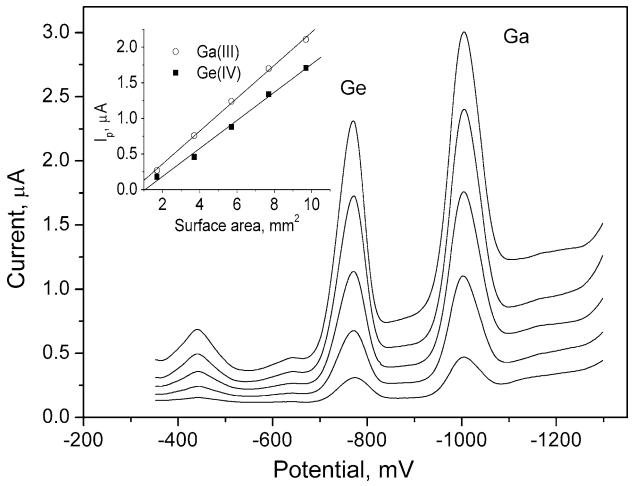

Fig. 5 Voltammograms obtained for electrode surface area: 1.7, 3.7, 5.7, 7.7, and 9.7 mm^2 for 20-nM gallium(III) and 40-nM germanium(IV) in 0.75-mM catechol and 0.1-M acetate buffer (pH of base electrolyte 4.8). All other conditions as in Fig. 1

1.71 μA. The parameters of the linear growth of peak current versus surface of working electrode for 20 nM of Ga(III) are: slope 0.231 ± 0.004 [μA mm^{-2}], intercept −0.100 ± 0.032 [μA], correlation coefficient $r = 0.998$; and for 40 nM of Ge(IV) are: slope 0.197 ± 0.009 [μA mm^{-2}], intercept −0.183 ± 0.054 [μA], and correlation coefficient $r = 0.994$. For further study, a 7.7-mm^2 surface area was applied.

3.6 Interferences

The examined ions, such as Mn(II), Pb(II), Cd(II), Bi(III), Sb(V), As(III) in a 100-fold excess (vs. Ge(IV)) did not interfere. However, it was observed that for Zn(II) ions in a 100-fold excess, interpretation of Ga(III) signal was very difficult. For Cu(II) ions in a 50-fold excess, the Ga(III) peak current decreased by 60% and Ge(IV) peak current by 50% and for 100-fold excess the Ga(III) peak current decreased by 70% and the Ge(IV) peak current decreased by 90%. For Fe(III) ions in a 10-fold excess, no interferences were observed. For 100-fold excess, no interferences for Ga(III) signal were observed, but Ge(IV) signal decreased by 15%, for 1000-fold excess, the Ga(III) signal decreased by 95% and the Ge(IV) signal by 95%. For V(V) ions in a 2-fold excess, no interferences for Ga(III) signal were observed, but Ge(IV) signal decreased by 10%, and for 10-fold excess, no interferences for Ga(III) signal were observed, Ge(IV) signal decreased by 80%, for 100-fold excess the Ga(III) signal decreased by 95% and the Ge(IV) signal decreased by 90%. For U(VI) in a 2-fold excess, the Ga(III) signal decreased by 5% and the Ge(IV) signal decreased by 15%, for 10-fold excess the Ga(III) signal decreased by 25% and the Ge(IV) signal decreased by 70%, and for 100-fold excess the Ga(III) signal decreased by 95% and Ge(IV) signal by 97%. For Sb(III) ions in a 10-fold excess, no interferences for Ga(III) signal were observed, but the Ge(IV) signal decreased by 40%, for 50-fold excess, and the Ga(III) signal decreased by 50% and the Ge(IV) signal by 95%. For Se(IV) ions in a 100-fold excess, the Ga(III) signal decreased by 50% and the Ge(IV) signal by 20%. Fortunately, the presence of most examined ions in water samples is very low. The examined ions such as Cu(II), U(VI), Sb(III), and Fe(III) caused serious interferences probably due to its possibility to complexes formation with catechol under proposed conditions. In the case of other examines ions only slight interferences were observed probably due to no intermetallic compounds formation with Ga(III) and Ge(IV) and low complexes formation with catechol.

The surface-active compounds are usually a source of strong interferences in voltammetric methods. A non-ionic surface-active compound (Triton X-100) and humic acid were investigated in this respect. A concentration of 0.1 mg L^{-1} for Triton X-100, decreased 20 nM of gallium signal by 14%, for 1 mg L^{-1} of Triton X-100 by 55% and for 5 mg L^{-1} of Triton X-100 by 97%. In the case of 40-nM germanium, a concentration of 0.1 mg L^{-1} Triton X-100 decreased signal by 3%, for 1 mg L^{-1} of Triton X-100 by 40% and for 5 mg L^{-1} of Triton X-100 by 90%. In the case of humic acid, a concentration of 0.1 mg L^{-1} decreased gallium signal by 35%, for 0.5 mg L^{-1} of humic acid by 80% and for 1 mg L^{-1} by 95%. In the case of germanium, a concentration of 0.1 mg L^{-1} humic acid decreased signal by 70%, for 0.5 mg L^{-1} of humic acid by

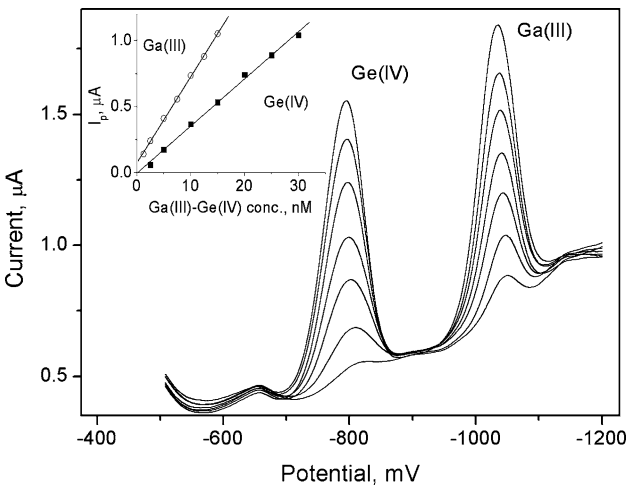

Fig. 6 *DPAdSV* gallium(III) and germanium(IV) calibration curves obtained for preconcentration time 30 s in 0.75-mM catechol and 0.1-M acetate buffer (pH of base electrolyte 4.8) and corresponding voltammograms. All other conditions as in Fig. 1

Table 1 Recovery and precision of the determination of trace gallium(III) and germanium(IV)

Added [nM]	Found [nM]	Recovery [%]	RSD [%]
Ga(III)			
1.25	1.4	112	4.7
3.5	3.3	94	4.3
11	10.6	96	4.2
Ge(IV)			
3	2.9	97	5.0
7	7.7	110	4.1
18	18.9	105	3.7

95% and 1 mg L^{-1} of humic acid was enough to suppress the signal completely. Consequently, surface active compounds should be thoroughly mineralized by digestion prior to analysis.

3.7 Analytical performance

The *DPAdSV* voltammograms of Ga(III) for the 1.25–15 nM and Ge(IV) for the 2.5–30 nM concentration range and preconcentration time of 30 s are presented in Fig. 6. For a short preconcentration time (30 s), the obtained detection limit for Ga(III) is 0.65 nM and the linearity is up to 90 nM (slope for regression line is 0.065 ± 0.001 [$\mu A\ nM^{-1}$], intercept 0.07 ± 0.04 μA, correlation coefficient 0.9991). The detection limit for Ge(IV) is 1.4 nM and the linearity is up to 170 nM (slope for regression line is 0.036 ± 0.001 [$\mu A\ nM^{-1}$], intercept -0.05 ± 0.14 μA, correlation coefficient 0.9982). A longer preconcentration time results in a lower detection limit. For example, for a preconcentration time of 60 s, the detection limit for Ga(III) is 0.36 nM and, for Ge(IV), the detection limit is 0.8 nM. The slopes for regression lines are [$\mu A\ nM^{-1}$]: 0.112 ± 0.002 and 0.734 ± 0.003 for Ga(III) and Ge(IV), respectively. Precision and recovery were determined using three different samples spiked of Ga(III) and Ge(IV) (Table 1).

The water and soil samples, spiked with gallium(III) and germanium(IV), were analyzed according to the described procedure using the Hg(Ag)FE electrode. Determination of Ga(III) and Ge(IV) was performed using the standard addition method. Results from Ga(III) and Ge(IV) determination are presented in Table 2. The recovery of Ga(III) ranged from 97 to 106% and germanium(IV) from 96 to 112%. The analytical usefulness of the presented method for the simultaneous determination of trace gallium(III) and germanium(IV) in samples was confirmed.

4 Conclusions

The presented *DPAdSV* method for the electrochemical simultaneous determination of gallium(III) and germanium(IV) with catechol using a cylindrical silver-based mercury film electrode Hg(Ag)FE, refreshed before each measurement, allows to determine Ga(III) and Ge(IV) at trace level, in concentrations as low as 25 and 58 ng L^{-1}, respectively, for a preconcentration time of 90 s. The reproducibility of the method is very good, i.e., when measured as RSD is 4.1% for Ga(III) and 3.7% for Ge(IV) (with each measurement performed at a fresh surface of the working electrode). Acceptable recovery (96–112%) shows that the proposed method can be used for the determination of Ga(III) and Ge(IV) in natural samples.

The obtained results confirm that method and Hg(Ag)FE may be in the future incorporated into out-of-laboratory sensor systems.

Table 2 Results of gallium(III) and germanium(IV) determination in natural samples

Added (nM)	Tap water (nM)	Rudawa river (nM)	Vistula river (nM)	Soil (ppm)
Ga(III) found $\bar{x} \pm s$ (recovery, %) {AAS}				
0	<DL	1.16 ± 0.10	0.91 ± 0.07	15.2 ± 0.6 {14.1 ± 0.9}
3	3.09 ± 0.08 (103)	3.99 ± 0.17 (96)	4.11 ± 0.19 (105)	–
6	5.82 ± 0.4 (97)	7.23 ± 0.26 (101)	7.12 ± 0.32 (103)	–
20 (ppm)	–	–	–	34.5 ± 1.1 (98)
Ge(IV) found $\bar{x} \pm s$ (recovery, %) {AAS}				
0	<DL	1.41 ± 0.12	<DL	2.14 ± 0.16 {2.7 ± 0.13}
3	3.03 ± 0.14 (101)	4.72 ± 0.18 (107)	2.85 ± 0.13 (95)	–
6	6.36 ± 0.34 (106)	7.56 ± 0.33 (102)	5.88 ± 0.25 (98)	–
2 (ppm)	–	–	–	4.31 ± 0.28 (104)

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