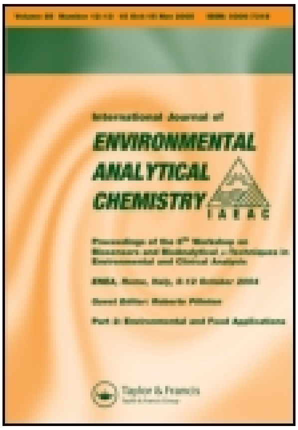

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Sensitive voltammetric determination of gallium in aluminium materials using renewable mercury film silver based electrode

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Simple cyclic renewable silver amalgam film electrode (Hg(Ag)FE), applied for the determination of gallium(III) using differential pulse anodic stripping voltammetry (DP ASV), is presented. The effects of various factors such as: preconcentration potential and time, pulse height, step potential and supporting electrolyte composition are optimised. The calibration graph is linear from 5 nM ($0.35\,\mu g\,L^{-1}$) to 80 nM ($5.6\,\mu g\,L^{-1}$) for a preconcentration time of 60 s, with correlation coefficient of 0.995. For a Hg(Ag)FE with a surface area of $9.9\,mm^2$ the detection limit for a preconcentration time of 120 s is as low as $0.1\,\mu g\,L^{-1}$. The repeatability of the method at a concentration level of the analyte as low as $3.5\,\mu g\,L^{-1}$, expressed as RSD is 3.2% ($n = 5$). The proposed method was successfully applied by studying the synthetic samples and simultaneously recovery of Ga(III) from spiked aluminium samples.

Keywords: gallium; aluminium materials; mercury film electrodes; 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 mobilisation and diffusion. Due to the latter application, world production is increasing and the level of gallium in the environment is beginning to rise, mainly around industrial areas [1,2].

Few analytical techniques possess the sensitivity required for trace and ultratrace quantification of gallium [3]. The most widely used techniques for the determination of gallium are atomic absorption spectrometry [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.

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The 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 a solution containing thiocyanate or salicyc 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. 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 means of adsorptive stripping voltammetry using salicyl fluorone [18], solochrome violet RS [19], ammonium pyrrolidine dithiocarbamate, pyrocatechol violet and diethyldithiocarbamate [20]. The method allowed to determine gallium(III) down to $80\,\mathrm{ng\,L^{-1}}$ for a 120 s preconcentration time when solochrome violer RS as a ligand was used [19].

Most voltammetric methods required mercury electrodes. The HMDE is the electrode of preference due to its high reproducibility and linearity. However, the toxicity of mercury limits the usage of the mercury electrodes in analytical practice and excludes them from 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 (Hg(Ag)FE). The principle of working and first proposal of a construction of the (Hg(Ag)FE) has been described by Baś and Kowalski [21]. The (Hg(Ag)FE) electrode was successfully applied for the determination of many metals and elemental sulphur [21–30].

In this work differential pulse anodic stripping voltammetry (DP ASV) is applied for the gallium(III) determination in KSCN and HCl. The procedure was examined and successfully utilised for determination of gallium(III) in aluminium foil food containers. The accuracy of the method was tested by studying the recovery of gallium(III) from spiked synthetic solutions and aluminium samples.

2. Experimental

2.1 *Measuring apparatus and software*

A multipurpose Electrochemical Analyser 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 amalgam film electrode (Hg(Ag)FE) [21], refreshed before each measurement and with a surface area of $1–12\,\mathrm{mm^2}$, as the working electrode, a double junction reference electrode Ag/AgCl/KCl (3M) with replaceable outer junction (3 M KCl) and a platinum wire as an auxiliary electrode. The pH measurements were performed using a laboratory pH-meter. Stirring was performed using a magnetic bar rotating at approximately 500 rpm. All experiments were carried out at room temperature.

2.2 *Construction of the cyclic renewable mercury film electrode Hg(Ag)FE*

The simple construction of the applied electrode that allows the mercury film to be refreshed before each measurement, a procedure essential for its performance, is given in Figure 1. The procedure of refreshing the outer mercury film involves two steps (Figure 1a)

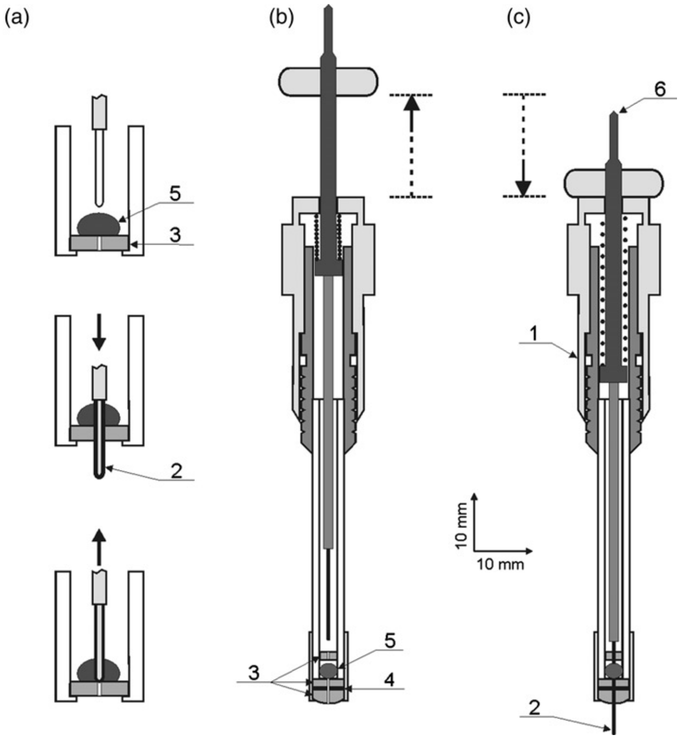

Figure 1. (a) The principle of mechanical refreshing of the mercury film silver based electrode. The Hg(Ag)FE used in our experiments: (b) configuration before use, (c) configuration ready for measurement. (1) micrometric screw, (2) piston pin with Ag cylindrical electrode at the end, (3) O-ring, (4) Ag foil (0.05 mm), (5) liquid silver amalgam (~10 µl), (6) electric contact pin.

pulling up the silver electrode base inside the electrode body, through the mercury chamber and then (Figure 1b) pushing it back outside the electrode body. During these movements, the silver wire base comes into contact with the liquid amalgam twice. The total volume of the liquid silver amalgam used to fill up the chamber does not exceed 10 µL. The silver amalgam was prepared by sinking several silver wires (0.5 mm diameter) in 0.5 mL of mercury (of analytical grade) for seven days to obtain saturated concentration of Ag. In comparison to pure mercury, the liquid amalgam allows the electrode to function in a stable manner for a great number of regeneration cycles (at least 2000, time of regeneration less than 1 s) and, furthermore, to stay usable for an extended period of several months. Usually after 2000 cycles, the whole silver/mercury amalgam from the chamber of Hg(Ag)FE was replaced.

2.3 *Chemicals and glassware*

All reagents used were of analytical grade (KSCN and HCl (Merck, Suprapur®), mercury GR for polarography (Merck)). The preparation of 0.01 M standard stock solutions of gallium(III) was achieved by dissolving Ga_2O_3 (Merck) in HCl (Merck, Suprapur®). Solutions with lower gallium concentrations were made weekly by appropriate dilution of the stock solution. Surfactants such as Triton X-100 (Windsor Laboratories, UK) and humic acid (sodium salt, Aldrich) were used. A 0.1% solution of humic acid was prepared by dissolving the primary (original) reagent in water distilled 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, UK). Prior to use, glassware was cleaned by immersion in a 1:1 aqueous solution of HNO_3, followed by copious rinsing in distilled from quartz water.

2.4 *Standard procedure of measurements*

Quantitative measurements were performed using differential pulse anodic stripping voltammetry (DP ASV) and the standard addition procedure. The procedure of refreshing the silver amalgam film Hg(Ag)FE was carried out before each measurement. A potential of −0.10 V was applied to cleaning the electrode. The Hg(Ag)FE conditioned in this way was used to determine gallium(III) in the supporting electrolyte: 0.01 M KSCN + 10 µL HCl (1:10) (total volume 10 mL) contained in a quartz voltammetric cell. The potential of the electrode was changed in the following sequence: cleaning potential −0.1 V for 10 s, accumulation potential $E_{acc} = -1.05$ V for $t_{acc} = 60$ s. During the accumulation step gallium(III) was collected while the solution was being stirred. Then, after a rest period of 5 s a differential pulse voltammogram was recorded in the anodic direction from −1.05 V to −0.55 V. The other experimental parameters were as follows: step potential, 4 mV; pulse potential, 25 mV; time step potential, 20 ms (10 ms waiting + 10 ms probing time). The measurements were carried out from deaerated solutions.

2.5 *Sample preparation*

For DP ASV determination of Ga(III) in aluminium samples, ~250 mg of metal samples were transferred directly into a volumetric flask (10 mL). For each sample, 4 mL of HCl (1:1) was added. After digestion the volumetric flasks were filled to the mark with distilled water.

3. Results and discussion

3.1 *Renewable Film Electrode Hg(Ag)FE*

Anodic stripping voltammetric techniques are applicable for measuring traces of gallium(III). Unfortunately preconcentration gallium as an amalgam at the mercury electrode suffers some problems: the low solubility of gallium in mercury, formation of intermetallic compounds with other metals such as copper and zinc. Additionally, efficiency of preconcentration of gallium at mercury drop electrode is poor and geometrical size of electrode is usually smaller than 3 mm^2. The Hg(Ag)FE is most devoid of the above mentioned limitations. Signals obtained for Hg(Ag)FE as compared to HMDE are found in Figure 2.

Gallium peak current is much higher (~16 times) for the Hg(Ag)FE vs. the HMDE (for geometrical sizes of surfaces of working electrodes 9.9 mm^2 – Hg(Ag)FE and 1.6 mm^2 – HMDE). Peak potential shifted to the more negative values at 40 mV for Hg(Ag)FE. The halfway width of the gallium(III) peak current was 31 mV for Hg(Ag)FE and 40 mV for HMDE. The background current is higher for Hg(Ag)FE. However signal to background

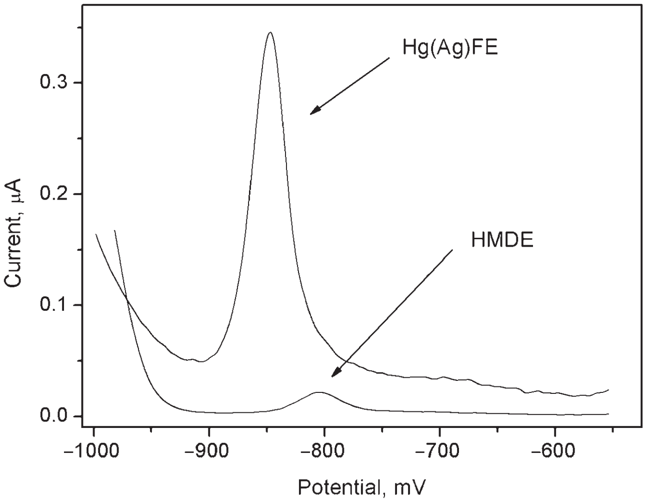

Figure 2. Comparison of voltammograms obtained for 50 nM gallium(III) in 0.01 M KSCN + 10 μL HCl 1:10 (pH of base electrolyte 3.05) for HMDE and Hg(Ag)FE electrode. The electrode areas were 9.9 mm^2 for the Hg(Ag)FE and 1.6 mm^2 for the HMDE. Instrumental parameters: $\Delta E = 25$ mV, $E_s = 4$ mV, t_w, $t_p = 10$ ms. Preconcentration potential $E_{acc} = -1.05$ V and time $t_{acc} = 60$ s. Stirring rate, 500 rpm.

current ratio is higher for Hg(Ag)FE (11-times) vs. HMDE (7-times) electrode. The obtained precision was 3.2% ($n = 5$). The surfaces of solid electrodes are usually much larger than those of mercury drop electrodes. When using the Hg(Ag)FE the surface of the working electrode may easily be varied in a wide range. For a surface area of 1.9 mm^2, the gallium peak current was 67 nA and grew linearly as the surface of the working electrode increased in size. For a surface area of 9.9 mm^2, the peak current was 333 nA. The parameters of the linear growth of peak current vs. surface of working electrode are: slope, 32.3 ± 1.8 [nA mm^{-2}], intercept, 16.8 ± 11.7 [nA] and correlation coefficient $r = 0.995$. For further study, the 9.9 mm^2 surface area because of advantageous signal to background current ratio was applied.

3.2 *Influence of DPV parameters on technique on gallium(III) peak*

The important parameters of the DPV technique are pulse amplitude (ΔE), potential step (E_s), waiting time (t_w) and probing time (t_p). Consequently, these parameters were investigated. To optimise the conditions for gallium measurements, the following instrumental parameters were systematically varied: ΔE in the range 5–75 mV (both positive and negative mode), E_s in the range 1–6 mV, t_w and t_p from 10 to 80 ms, respectively.

For a pulse amplitude of 5 mV the gallium(III) peak current was equal to 56 nA and increased with increasing pulse amplitude. The best results were obtained for an amplitude of 25 mV (the peak current was ~290 nA). Higher pulse amplitude (>25 mV) caused major growth of the halfway width of the peak. The increase in pulse amplitude from 5 to 75 mV caused the peak potential to shift from −843 to −894 mV and from −822 to −818 mV for negative pulse amplitude respectively (peak currents were similar for positive and negative mode). For further work, the pulse amplitude of 25 mV was applied.

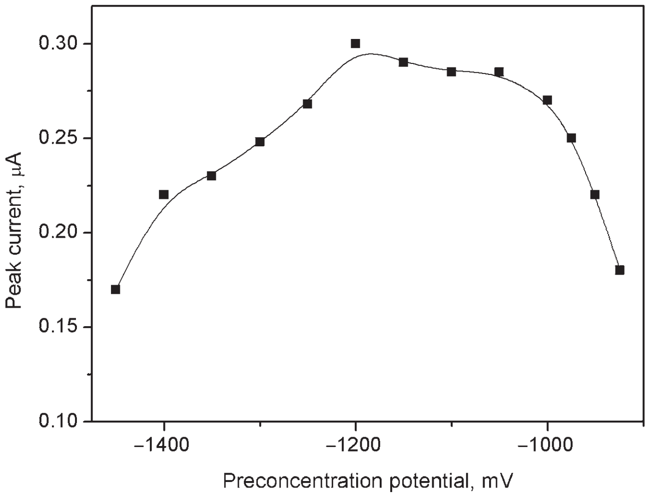

Figure 3. Dependence of the peak current on preconcentration potential in the range from −925 to −1450 mV for 50 nM gallium(III) in 0.01 M KSCN + 10 μl HCl 1:10 (pH of base electrolyte 3.05). All other conditions as in Figure 1.

Changes of the step potential cause influence on peak current. For a step potential equal to 1 mV the peak current was 103 nA, and for a step potential of 6 mV the peak current was ~342 nA. Higher step potential than 4 mV cause major increase in a background current (Ga(III) signal to background current ratio is lower). The step potential of 4 mV was applied in further work.

The waiting time and probing time were changed in the range from 10 to 80 ms. The best result was obtained for waiting time and probing time of 10 ms, and this was the value chosen for further work.

3.3 *Influence of preconcentration potential and time on gallium(III) peak*

Influence of preconcentration potential and time are always important factors on the sensitivity and detection limit of the method. Optimal preconcentration potential for gallium(III) determination in KSCN and HCl (pH of base electrolyte 3.05) is in the range from −1.05 to −1.20 V (Figure 3). For preconcentration potentials lower than −1.05 V and higher than −1.20 V, the gallium peak decreased significantly. Because of interference from zinc, for further work a −1.05 V preconcentration potential was applied.

The changes in magnitude of the gallium current vs. preconcentration time are presented in Figure 4. The peak current increased with the increase of the preconcentration time from 75 nA (t_{acc} = 15 s) to 475 nA (t_{acc} = 300 s). For a preconcentration time higher than 180 s, practically no increase of the gallium peak current was observed.

3.4 *Influence of pH on gallium(III) peak*

Determination of gallium in presence KSCN requires acidic conditions. The peak current of Ga(III) depends on the pH. In Figure 5, the dependence of peak current on pH

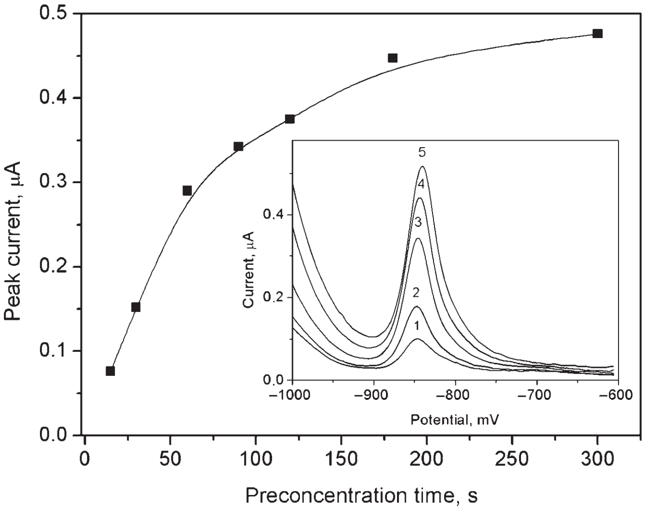

Figure 4. Dependence of the peak current on preconcentration time in the range from 15 to 300 s for 50 nM gallium(III) in 0.01 M KSCN + 10 μl HCl 1:10 (pH of base electrolyte 3.05) and obtained voltammograms for (1) – 15; (2) – 30; (3) – 60; (4) – 120 and (5) – 300 s of preconcentration time. All other conditions as in Figure 1.

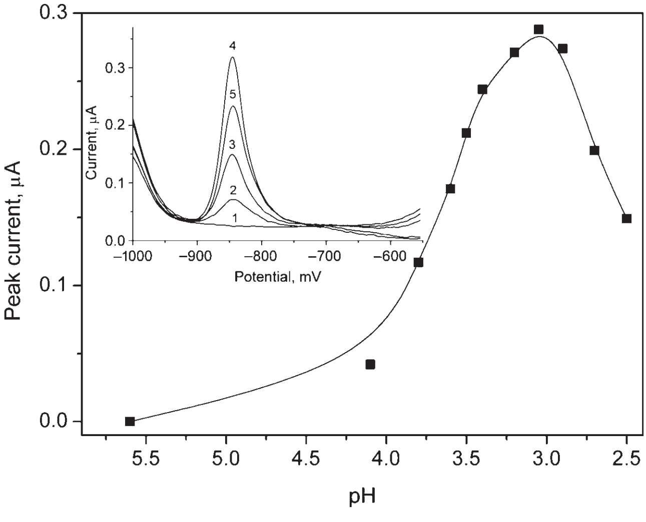

Figure 5. Dependence of the peak current on pH in the range from 5.6 to 2.5 for 50 nM gallium(III) in 0.01 M KSCN + HCl 1:10 + obtained voltammograms for pH of (1) – 5.6; (2) – 4.1; (3) – 3.8; (4) – 3.5 and (5) – 3.05. All other conditions as in Figure 1.

is presented. For a pH of 5.6 no gallium peak was observed. For a pH of 4.1, the observed gallium peak current was 41 nA and increased with lower pH. The optimal pH was for 3.05 (with the peak current reaching values about 290 nA). More acidic conditions caused a decrease in the peak current, e.g. for a pH of 2.5 the peak current was 147 nA. For further measurements, the pH of 3.05 was applied.

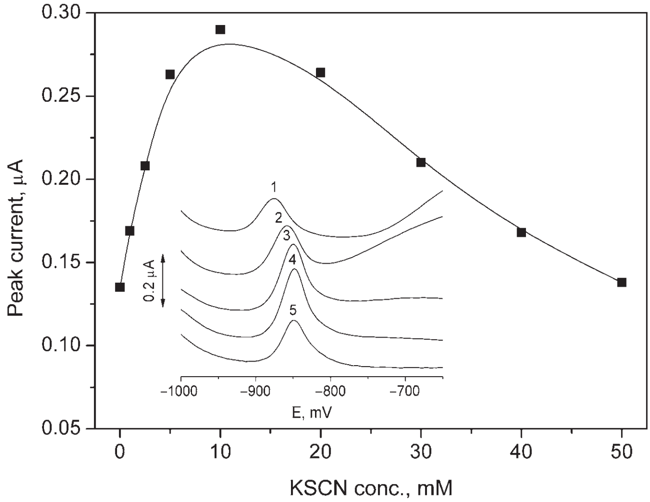

Figure 6. Dependence of the peak current on KSCN concentration in the range from 0 to 50 mM for 50 nM gallium(III) + 10 μl HCl 1:10 and obtained voltammogrms for (1) – 0; (2) – 1; (3) – 2.5; (4) – 10; (5) – 50 mM of KSCN. All other conditions as in Figure 1.

3.5 *Influence of KSCN concentration on gallium(III) peak*

As a supporting electrolyte KSCN was used [16]. The gallium(III) peak current and its potential depend on the concentration of KSCN (Figure 6). The addition of KSCN to the base electrolyte is accompanied by increase of the Ga(III) peak. The best result was obtained for 0.01 M of KSCN (with the peak current reaching values about 0.3 μA). Higher concentrations of KSCN cause decrease in the peak current. The concentration of KSCN also had an influence on the peak potential, which changed to more positive values for higher KSCN concentrations, e.g. for 0 M of KSCN the peak potential was −874 mV and for 0.05 M of KSCN the peak potential was −846 mV. For further work, a concentration of 0.01 M was used.

3.6 *Interferences*

For the 50 nM of Ga(III) the examined ions such as Pb(II), Cd(II), Tl(I), Mn(II), Se(IV), In(III), Bi(III), Ge(IV), Th(IV), U(VI), Mo(VI) in a 20-fold excess did not interfere. However, it was observed that for Sb(III) ions in a 10-fold excess, the Ga(III) peak current decreased by 30% and for 20-fold excess decreased by 40%. For Zn(II) ions in a 10-fold excess the Ga(III) peak current decreased by 8%, for 20-fold excess decreased by 15% and for 50-fold excess decreased by 35%. For Cu(II) ions in a 1-fold excess, the Ga(III) peak current decreased by 30%, for 10-fold excess decreased by 90% and for 20-fold excess decreased completely (no Ga(III) signal was observed). For Fe(III) ions in a 100-fold excess the Ga(III) peak current decreased by 5% and for 1000-excess decreased by 70%. Unfortunately ions such as Zn(II), Cu(II) and Fe(III) are commonly present in natural samples. The interferences from Cu(II) and Zn(II) could be easily eliminated by the addition to the supporting electrolyte sodium diethylenedithiocarbamate (100-fold excess vs. concentration of present ion). Addition of 25 μM of sodium diethyldithiocarbamate to

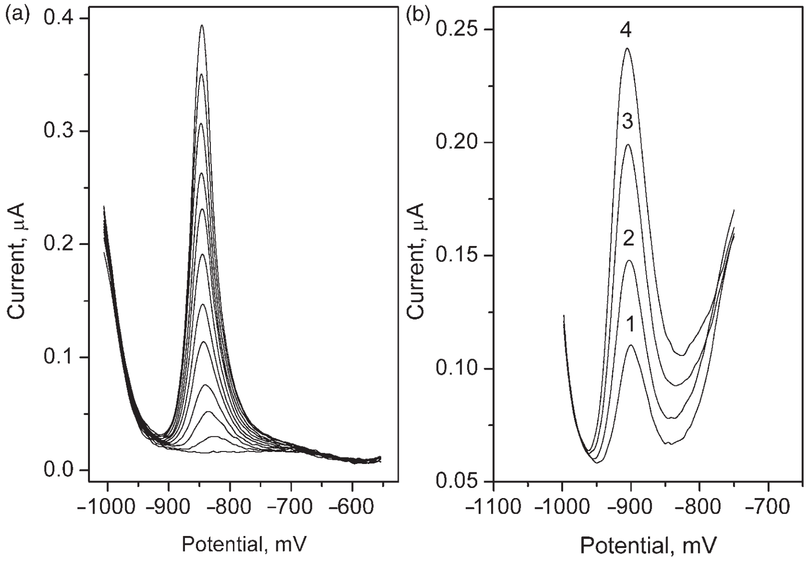

Figure 7. (a) – DP ASV gallium(III) calibration voltammograms from 0 to 55 nM Ga(III) obtained for preconcentration time 60 s in 0.01 M KSCN + 10 μl HCl 1:10 (pH of base electrolyte 3.05). (b) – Ga(III) voltammograms obtained for aluminium can sample (1) and (2) – 5; (3) – 10; (4) – 15 nM of Ga(III). All other conditions as in Figure 1.

the supporting electrolyte have no influence on the analytical signal Ga(III). However, it was observed that for 50 μM DDTC the Ga(III) signal decreased by 5% and for 100 μM DDTC by 25%. Peak potential shifted to more negative values of 20 mV and the halfway width of the gallium(III) peak increased by 15 mV for 100 μM DDTC. To mask the interferences from Zn(II) and Cu(II) ions, a 25-fold excess and 75-fold excess of DDTC were required. If both Cu(II) and Zn(II) ions are present, the 100-fold excess of DDTC was required. The DDTC should be introduced to the supporting electrolyte simultaneously with the sample. In practical application DDTC was added to the moment when gallium peak was well defined and Zn(II) and Cu(II) signals were eliminated. Time required to mask Zn(II) and Cu(II) ions was no longer than 5 min. In the case of Fe(III) ions addition to the supporting electrolyte F^- ions eliminates interferences.

3.7 *Analytical performance*

The DP ASV voltammograms of Ga(III) for the 0–55 nM concentration range and preconcentration time of 60 s are presented in Figure 7. For a preconcentration time of 60 s the obtained detection limit is 2.4 nM and the linearity is up to 80 nM (slope for regression line is 7.15 ± 0.47 [nA nM^{-1}], intercept −44.7 ± 16 [nA], correlation coefficient 0.995). A longer preconcentration time results in a lower detection limit. For example, for a preconcentration time of 120 s the detection limit is 1.5 nM. The slope for regression line is 12.3 ± 0.7 [nA nM^{-1}], intercept −32.2 ± 23.6 [nA] and correlation coefficient 0.994. Precision and recovery were determined using three different samples spiked by 5, 12.5 and 18 nM of Ga(III) (Table 1).

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

Added [nM]	Found [nM]	Recovery [%]	RSD [%]
5	4.7	94	5.1
12.5	12.1	97	4.2
18	18.2	101	3.3

Table 2. Results of gallium(III) determination in the aluminum samples.

Ga(III) added ($\mathrm{mg\,kg^{-1}}$)	Ga found $\bar{x} \pm s$ (recovery, %) {AAS} [$\mathrm{mg\,kg^{-1}}$]		
	Aluminium can	Aluminium foil	Aluminium foil container
0	8.94 ± 0.49 {10.1 ± 0.4}	24.3 ± 1.7 {24.9 ± 1.2}	33.1 ± 2.2 {30.2 ± 2.6}
5	14.1 ± 0.57 (104)	–	–
10	18.6 ± 0.63 (98)	32.6 ± 1.9 (95)	42.7 ± 1.4 (99)
20	–	43.5 ± 2.1 (96)	54.2 ± 1.9 (102)

The aluminium samples, spiked with gallium(III), were analysed according to the described procedure using the Hg(Ag)FE. Determinations of Ga(III) were performed using the standard addition method. Results from Ga(III) determination are presented in Table 2. The recovery of Ga(III) ranged from 93 to 104%. Obtained results are in good agreement with AAS method. The analytical usefulness of the presented method for the determination of gallium(III) in samples was confirmed.

4. Conclusions

The presented DP ASV method for the electrochemical determination of gallium(III) using a cylindrical silver amalgam film electrode (Hg(Ag)FE), refreshed before each measurement, allows one to detect Ga(III) in concentrations as low as 1.5 nM (0.1 $\mu\mathrm{g\,L^{-1}}$) for a preconcentration time of 120 s. The proposed method gives comparable detection limit to the method reported by Wang and Zadeii [19] and is about one order magnitude lower than the other ASV method. The reproducibility of the method is good, i.e. when expressed as RSD is 3.2% (with each measurement performed at a fresh surface of the working electrode). Acceptable recovery (93–104%) shows that the proposed method can be used for the determination of Ga(III) in aluminium samples. Interferences from typical metals such as Zn, Cu, Fe can easily be removed.

The simple, mechanical system of mercury film refreshing provides a good surface electrode repeatability and reproducibility that is not available for other mercury film electrodes. The miniature construction of the device and possibility of automation of the process indicate that the Hg(Ag)FE may be especially useful in flow measurements conditions. With the Hg(Ag)FE, the disadvantages of the HMDE (low surface area, poor mechanical resistance, susceptibility to damage and the application of mercury in measurements etc.) may be eliminated to a large degree.

The Hg(Ag)FE refreshed before each measurement demonstrates many properties which are specific only to the hanging mercury electrode. The Hg(Ag)FE displays long-term stability for at least 2–3 months.

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

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