

Possibilities of Simultaneous Determination of Indium and Gallium in Binary InGa Alloys by Anodic Stripping Voltammetry in Acetate Buffer

L. MEDVECKÝ and J. BRIANČIN

*Institute of Materials Research, Slovak Academy of Sciences, SK-043 53 Košice
e-mail: medvecky@imrnov.saske.sk*

Received 30 August 2002

Indium and gallium can be simultaneously determined by the thin-film anodic stripping voltammetry at Bi or HgBi thin-film electrode generated *in situ* on glassy carbon electrode. The Hg TFE is not suitable for determination, namely gallium ions at higher concentrations. From experiments it results that the height of indium peak is strongly influenced by the concentration of gallium ions in analyzed solution. As it was found, indium competes with bismuth and gallium with mercury for surface sites on glassy carbon electrode.

The simultaneous indium and gallium determination by anodic stripping voltammetry has not yet been studied. InGa alloys (in the liquid state) are currently used as conductive electrodes in measurements of physical properties, *e.g.* semiconductivity of ceramics because of low ohmic contacts between alloy and surface of ceramics. It results from the above mentioned that there is a real possibility of the need for a similar type of determination.

Both the anodic stripping voltammetry and polarography are very sensitive and powerful electroanalytical techniques for gallium determination, while analyses using a complex agent such as thiocyanate or salicyl acid appear to be the most suitable [1, 2]. Besides anodic stripping voltammetry, the adsorption voltammetry with morin as a complexing ligand can be also used [3] for the determination. A high concentration of Ga(III) ions ($> 10^{-4}$ mol dm $^{-3}$) in 0.1 M-NaClO $_4$ electrolyte was necessary in order to achieve any Ga signal. However, it was found that the signal intensity rose with acidity of analyzed solution [4]. An intensive gallium signal has been obtained in 0.1 M-acetate buffer [5]. Ga(III) ions, in the form of sodium gallate solution, can be reduced even from strong alkaline solutions, which is utilized to form the gallium-film electrode [6]. The composition of the supporting electrolyte has an important influence on the determination of In(III) by anodic stripping voltammetry at a thin-film electrode (TFE) [7]. It has been found that indium anodic stripping peak decreases with the amount of HCl in analyzed solution, while in 1 M-HCl it was not observed [8]. The results showed that there was no reduction and deposition of In(III) ions at mercury-film electrode in 1 M-HCl and consequently indium is not stripped into solution in the oxidation

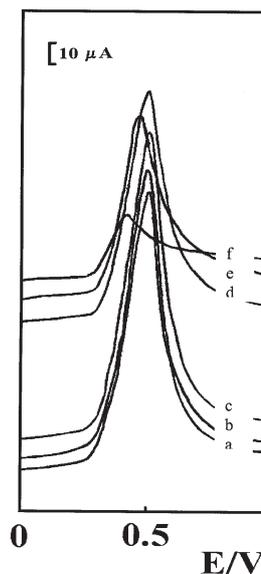


Fig. 1. Influence of gallium and indium ions concentrations in solution on mercury deposition on glassy carbon RDE. In(III) ions concentration (a) 1000, b) 2000, c) 3000 $\mu\text{g dm}^{-3}$) and Ga(III) ions concentration (d) 500, e) 1000, f) 1500 $\mu\text{g dm}^{-3}$).

step. The acetate—bromide electrolyte was chosen as the most suitable one for In(III) determination by adsorptive stripping voltammetry because the indium peak heights are the most reproducible [9]. In the case of very thin mercury films at glassy carbon electrodes, the whole surface of electrode may not be coated with mercury. This effect can cause reduction and stripping of deposited indium with substantial overpotential, which results in the decrease of the indium peak.

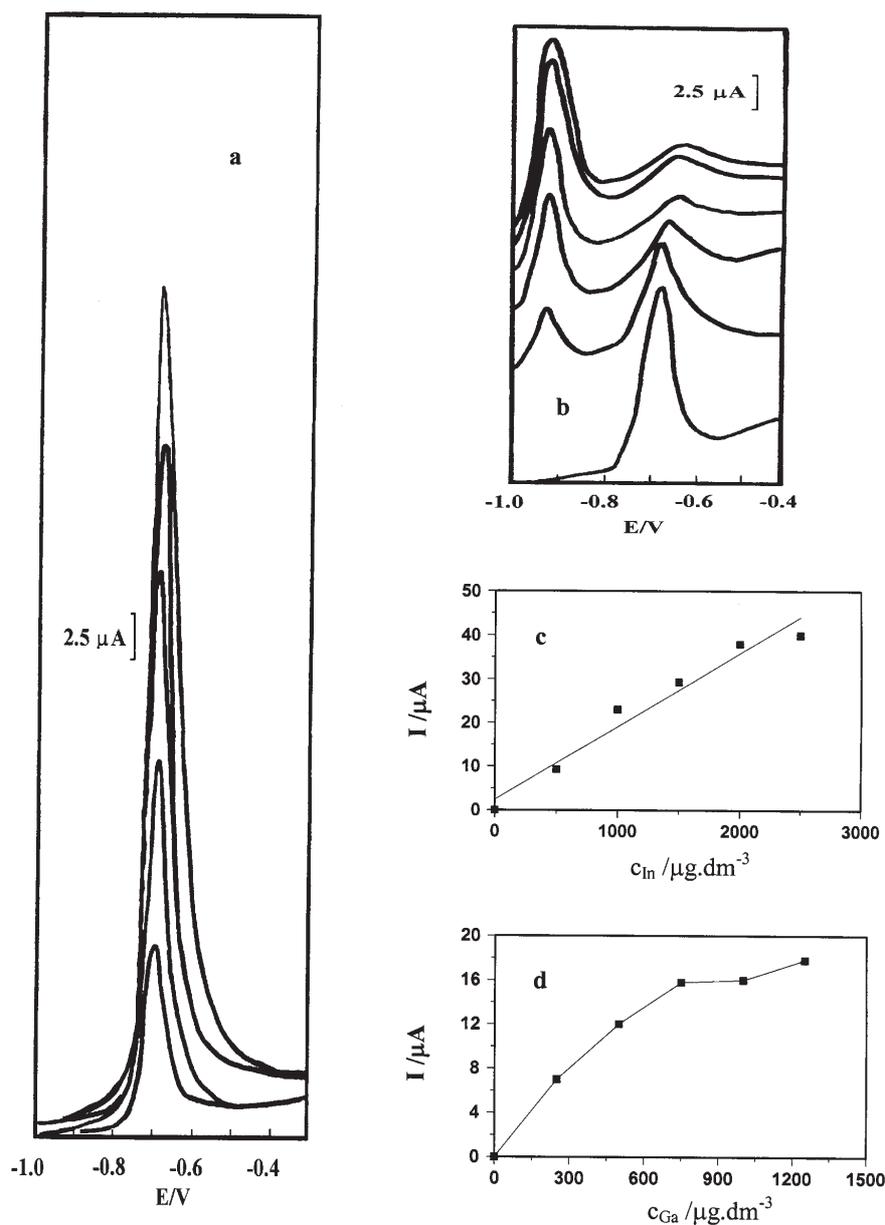


Fig. 2. Stripping voltammograms at mercury-coated glassy carbon RDE for indium solutions of increasing concentrations in $500 \mu\text{g dm}^{-3}$ steps (a) and the resulting calibration plot (c). Influence of gallium ions concentration in solution on height of indium peak (b) and calibration plot for gallium (d).

The optimum thickness of the mercury film on glassy carbon electrodes (to maintain a reproducible height of the anodic peak) was in the region from 10 nm to $5 \mu\text{m}$ [10]. In(III) ions can also be determined by the adsorptive stripping voltammetry at bismuth film electrode in a wide region of concentrations with the linear dependence of peak height on the concentration of indium ions [11].

In this paper, we have studied possibilities of the simultaneous determination of In and Ga by square-wave anodic stripping voltammetry (SWASV) at mercury, bismuth, and mixed mercury-bismuth thin-film electrodes that were generated *in situ* on a glassy carbon

rotating disc electrode without using complexing agents. From above reports it follows that the most sensitive and reproducible analysis of given elements can be achieved in acetate electrolyte with a low concentration of HCl. This fact was taken into account in the choice of electrolyte for analysis.

EXPERIMENTAL

The stock solutions of indium, gallium, and bismuth were prepared by dissolution of metallic In (99.99 % purity), Ga (99.9 % purity), and Bi (99.99 % purity) in 10 cm^{-3} of HNO_3 (60 %, anal. grade). The

standard solution of mercury was prepared by dissolution of HgO (anal. grade) in concentrated HNO₃ and all solutions were diluted with distilled water. A 0.1 M solution of sodium acetate was used as the supporting electrolyte.

The SWASV voltammograms were recorded using polarographic analyzer PA3 (Laboratorní přístroje Prague, Czechoslovakia) equipped with a rotating glassy carbon disc electrode (RDE, 3 mm in diameter), where glassy carbon electrode was *in situ* coated with the film of target metal (Hg, Bi, HgBi amalgam). The auxiliary electrode was a platinum foil and a saturated calomel electrode was used as the reference electrode. The glassy carbon electrode was polished with a diamond paste (< 1 μm particle size) before analysis. The voltammograms were recorded by applying a positive-going square-wave potential scan with a frequency of 10 Hz, modulation amplitude of 50 mV, and scan rate of 100 mV s⁻¹ or 20 mV s⁻¹. The analysis was performed in a 100 dm³ electrochemical cell containing 0.1 M-acetate buffer, the concentration of mercury was 3 × 10⁻⁴ mol dm⁻³ and the concentration of bismuth was 2.5 × 10⁻⁴ mol dm⁻³. The metals were deposited on RDE in a preconcentration step at the potential of -1.4 V for 90 s. After metal deposition, the stirring was stopped and after 10 s the voltammogram was recorded to potentials of 1.0 V (mercury thin-film electrode) or 0.35 V (bismuth thin-film electrode) with 45 s clearing step at these potentials (in figures are shown interesting parts of records from the point of view of the analyzed elements only).

RESULTS AND DISCUSSION

Fig. 1 shows the influence of Ga and In ions on the mercury peak height, and hence on the thickness of the deposited Hg film on RDE. The mercury peak height does not change with concentration of In(III) ions (curves *a–c*). A different situation can be seen in curves *d–f*, where approximately 20 % decrease in the Hg peak height is visible at 4 × 10⁻⁶ mol dm⁻³ Ga(III) ions in the solution and this height decreases approximately by about 25 % of the original Hg peak height at concentration of 1.2 × 10⁻⁵ mol dm⁻³ of Ga(III) ions. In anodic stripping, the dependence of In peak height on concentration of In(III) ions in the solution was almost linear (Figs. 2*a–c*). The correlation coefficient was 0.981 and the slope was 16.7 nA (μg dm⁻³)⁻¹. Each point of the relationship (this applies to all the calibration curves presented in the work) was measured three times, where the relative standard deviations (RSD) of measurements were < 6.3 %. The relationship between the Ga peak height and the concentration of Ga ions is linear up to 500 μg dm⁻³ Ga(III) and it does not change with further concentration increase (Fig. 2*b*). It is evident from the mentioned (see Fig. 1) that during deposition (reduction step) of individual metals on the electrode surface, Hg

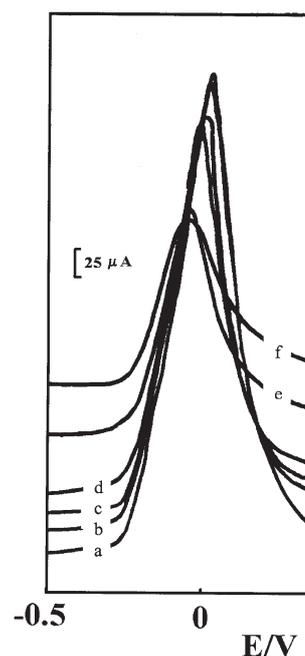


Fig. 3. Influence of gallium and indium ion concentrations in solution on bismuth deposition on glassy carbon RDE. Ga(III) ions concentration (*a*) 0, *b*) 500, *c*) 1000, *d*) 2000 μg dm⁻³ and In(III) ions concentration (addition of *e*) 1000, *f*) 2000 μg dm⁻³ In ions to solution containing 2000 μg dm⁻³ gallium).

and Ga ions compete for surface sites on the RDE. Ga ions are reduced faster than Hg ions and consequently the number of unoccupied sites on glassy carbon electrode surface that can be utilized for mercury electrodeposition from the solution decreases. This fact is also supported by the measured dependence in Fig. 2*b*, which shows that with an increase of the amount of deposited gallium on the electrode surface the In peak height significantly decreases during anodic stripping, which is in accordance with the observed decrease of the electrodeposited amount of mercury. Thus, the formation of In amalgam is inhibited with decreasing of the amount of electrodeposited mercury on RDE.

The influence of the concentrations of Ga and In ions on the bismuth deposition on the electrode surface is shown in Fig. 3. The Bi peak height decreases with the concentration of Ga ions substantially less (curves *a–d*) than in case of Hg TFE, however, by adding In(III) ions into the analyzed solution a significant decrease in the Bi peak height takes place (curves *e, f*). In this case, a similar phenomenon can be observed as in the case of Ga and Hg deposition; however, here In and Bi ions compete. It should be noted that the mechanism of simultaneous deposition of the respective pair of metals was a little influenced by activity and nature of surface sites on glassy carbon electrode since the same surface of electrode was used for metal deposition. Despite this fact, individual metal ions behave differently in the reduction step.

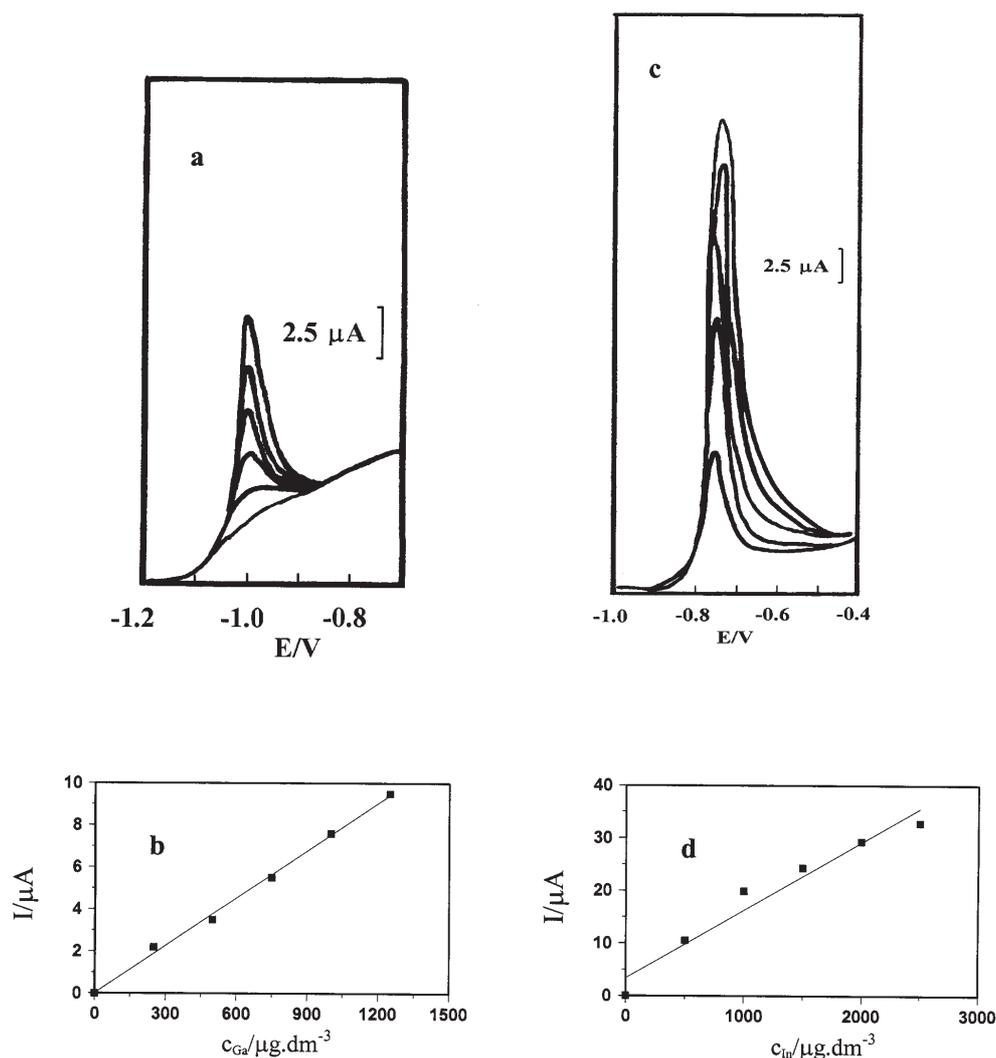


Fig. 4. Stripping voltammograms at bismuth-coated glassy carbon RDE for gallium and indium solutions of increasing concentrations in $250 \mu\text{g dm}^{-3}$ steps for Ga (a) and in $500 \mu\text{g dm}^{-3}$ steps for In (c), the resulting calibration plot for gallium (b) and indium (d).

The interaction of individual metal ions and the formation of transition surface states on the electrode surface probably play an important role in the reduction process. From the relationships shown in Figs. 4a, b it can be stated that a linear dependence of the Ga peak on Ga(III) ions concentration in the solution was observed (linear regression correlation coefficient (R) is 0.998, the slope (a) is $7.5 \text{ nA } (\mu\text{g dm}^{-3})^{-1}$, RSD < 7.5 %) and the relationship between the In peak height and the In(III) concentration without the presence of Ga ions in solution (Figs. 4c, d) is slightly curved at the higher concentrations, which is evident from the decreased value of $R = 0.976$ ($a = 12.8 \text{ nA } (\mu\text{g dm}^{-3})^{-1}$, RSD < 8.0 %). The influence of the Ga(III) concentration on the In peak height is shown in Fig. 5a. The In peak height markedly decreases with an increase of the concentration of Ga ions in the solution, while the deposited amount of Bi does not change with the concentration of Ga ions. This dependence is

very similar to that found out in the case of Hg TFE. The relationship between the Ga peak height (at a constant In(III) content in the solution) and the Ga concentration (Fig. 5b) is curved ($R = 0.963$, $a = 12.5 \text{ nA } (\mu\text{g dm}^{-3})^{-1}$, RSD < 7 %), which gives evidence of mutual Ga-In influence in the reduction process on this electrode. The presence of indium is acting on the Ga deposition in an inhibitive way. The Ga peak height increases with the concentration of In ions approximately three times its original value up to the concentration of In(III) ions of *ca.* $2000 \mu\text{g dm}^{-3}$ and then it changes only little (Fig. 5c); at the same time (Fig. 5d) the linearity of the relationship between the In peak height and the In(III) concentration improves at a constant concentration of Ga ions (respectively by the presence of Ga ions in solution) in the solution ($R = 0.997$, $a = 12.2 \text{ nA } (\mu\text{g dm}^{-3})^{-1}$, RSD < 6.5 %).

Fig. 6 shows the influence of the concentrations of Ga and In ions on the deposition of the BiHg film on

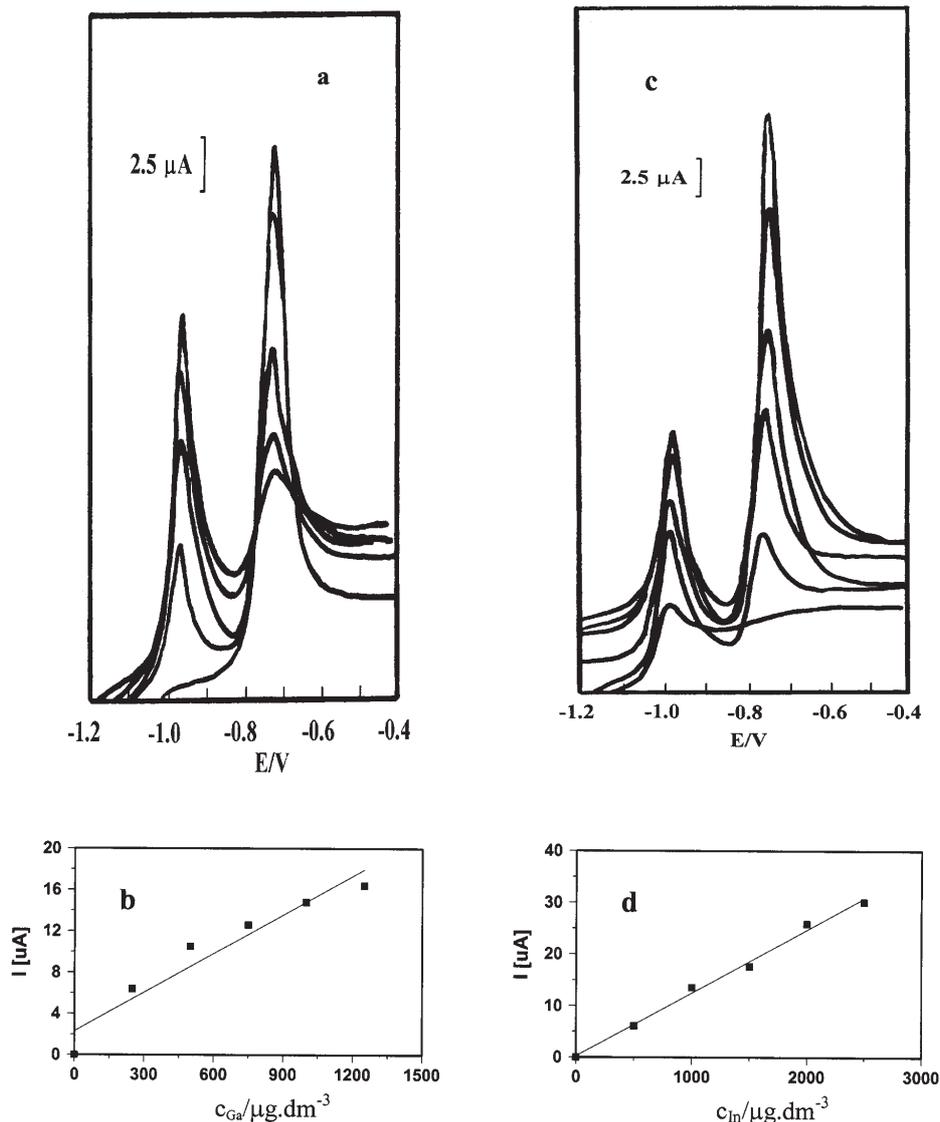


Fig. 5. Influence of gallium ions concentration in solution on height of indium peak (*a*, Bi TFE, at constant In concentration in solution of $1000 \mu\text{g dm}^{-3}$ and increasing concentration of Ga in $250 \mu\text{g dm}^{-3}$ steps) and resulting calibration plot for gallium (*b*). Influence of indium ions concentration in solution on height of gallium peak (*c*, Bi TFE, at constant Ga concentration in solution of $500 \mu\text{g dm}^{-3}$ and increasing concentration of In in $500 \mu\text{g dm}^{-3}$ steps) and resulting calibration plot for indium (*d*).

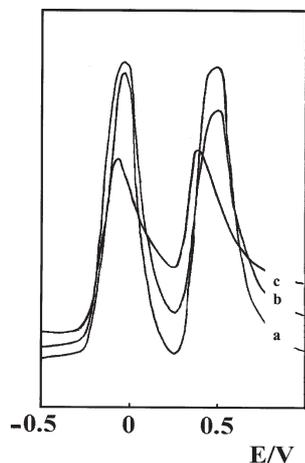


Fig. 6. Influence of gallium ions concentration in solution on simultaneous mercury and bismuth deposition on glassy carbon RDE. (*a*) $500 \mu\text{g dm}^{-3}$, (*b*) $1000 \mu\text{g dm}^{-3}$, and (*c*) $2000 \mu\text{g dm}^{-3}$ of Ga in solution).

the surface of a glassy carbon electrode. The height of both Hg and Bi anodic peaks decreases with the increasing concentration of Ga ions in the solution and the concentration of In ions does not influence their heights. The height of the Ga anodic peak increases linearly with its concentration in the solution (Figs. 7*a*, *b*) without the presence of In(III) ions in solution ($R = 0.999$, $a = 25.4 \text{ nA } (\mu\text{g dm}^{-3})^{-1}$, $\text{RSD} < 4 \%$), and in case of the same relationship for In ions (Fig. 7*c*, *d*) the linear dependence was also observed ($R = 0.991$, $a = 19.1 \text{ nA } (\mu\text{g dm}^{-3})^{-1}$, $\text{RSD} < 4.5 \%$). The increase of the concentration of Ga(III) ions in the solution (respectively their presence) markedly changes the shape of In anodic peak (Fig. 8*a*), and at concentrations $> 500 \mu\text{g dm}^{-3}$ Ga(III) the broad-

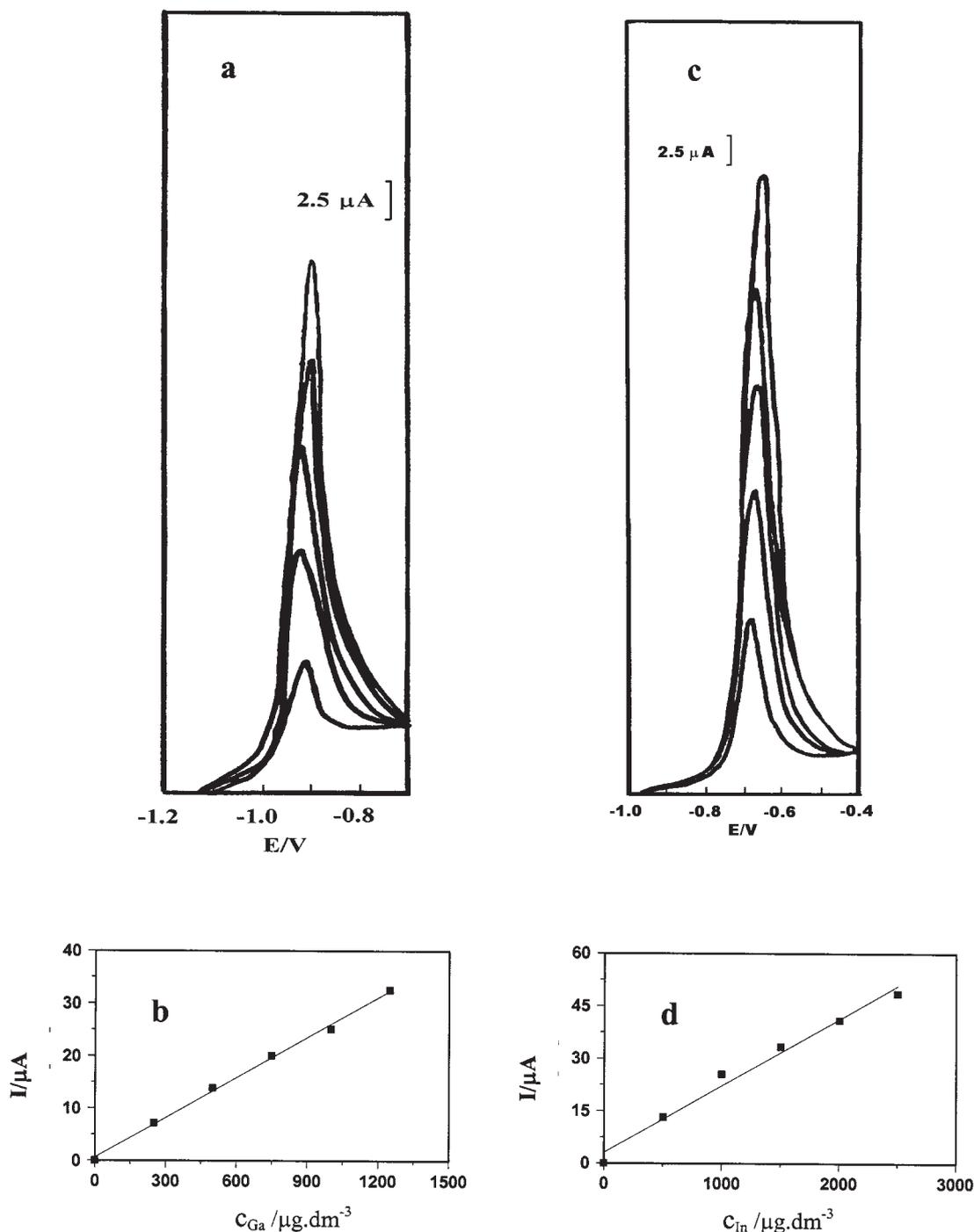


Fig. 7. Stripping voltammograms at HgBi-coated glassy carbon RDE for gallium and indium solutions of increasing concentrations in $250 \mu\text{g dm}^{-3}$ steps for Ga (a) and in $500 \mu\text{g dm}^{-3}$ steps for In (c), the resulting calibration plot for gallium (b) and indium (d).

ening of the In peak and its splitting takes place with a simultaneous decrease of its height to less than half of its original value. At the same time it should be stated that the linearity of the dependence of the Ga peak height on Ga(III) ions concentration (at a constant concentration of In(III) ions equal $1000 \mu\text{g dm}^{-3}$, Fig. 8b) was kept ($R = 0.999$) and similarly the value of slope ($a = 28.2 \text{ nA } (\mu\text{g dm}^{-3})^{-1}$, RSD <

7 %) was comparable to that observed in Fig. 7a. The presence of $500 \mu\text{g dm}^{-3}$ Ga(III) ions had no influence on the linearity of the relationship between the In peak height and the concentration of In(III) ions in the solution ($R = 0.998$, $a = 13.2 \text{ nA } (\mu\text{g dm}^{-3})^{-1}$, RSD < 2.5 %) despite its splitting (or broadening) (Fig. 8c, d). However, with an increase of the content of In ions (up to $2500 \mu\text{g dm}^{-3}$) the Ga peak height increases by

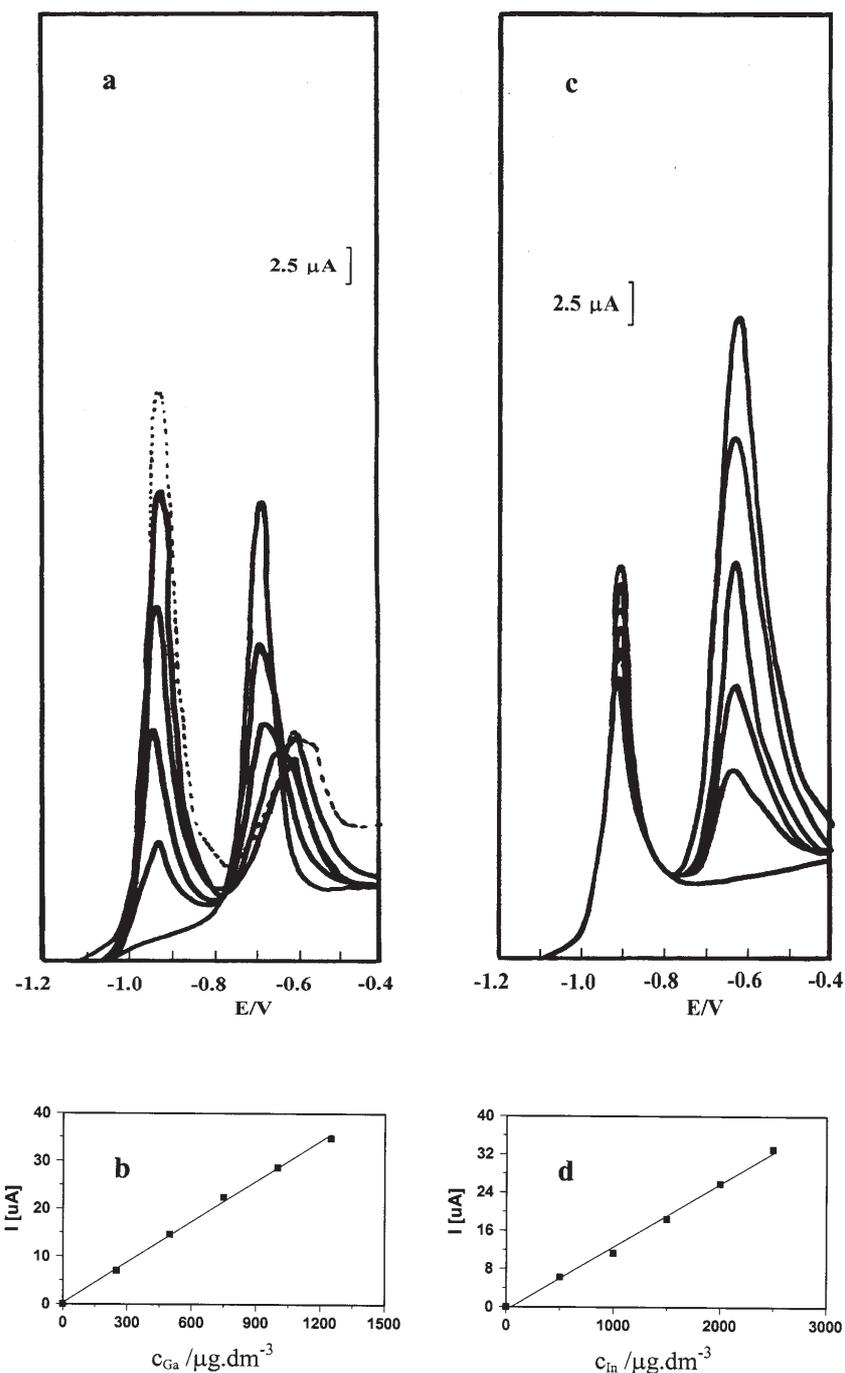


Fig. 8. Mutual influence of indium and gallium on the height of their anodic stripping peaks at HgBi TFE. (a) Influence of gallium ions concentration in solution on height of indium peak and resulting calibration plot for gallium (b), (c) influence of indium ions concentration in solution on height of gallium peak and resulting calibration plot for indium (d).

approximately 25 % of original peak height (Fig. 8c).

It clearly results from the measured dependences that Ga ions are preferably reduced on the surface of a glassy carbon electrode and competition with mercury ions causes the decrease of amalgam formation. At higher concentrations of Ga(III) ions ($> 8 \times 10^{-6} \text{ mol dm}^{-3}$) the electrode surface is coated with less than 25 % of original mercury amount. The reason for such behaviour of gallium and mercury can be small

mutual dissolubility of the mentioned metals and great differences in the nature of surfaces of individual drops of these metals. In case of Bi TFE, an opposite relationship between the deposition of gallium and indium in competition with bismuth than in the case of Hg TFE was found out, since Ga and Bi are mutually little dissoluble and consequently they should markedly influence each other during reduction, which was not observed. Instead of such a relationship, a decrease

of the Bi peak height with the In(III) concentration in the solution at a constant concentration of Ga(III) ions was observed, while according to phase diagrams [12] In and Bi are mutually considerably dissoluble (≈ 20 mass %). The mutual dissolubility of individual metals of the alloy probably does not represent a crucial criterion for the formation of the alloy and the electrodeposition of the respective layer.

CONCLUSION

Bi TFE or HgBi TFE are the most suitable electrodes for simultaneous determination of In and Ga in their alloys in the acetate buffer without using of complexing agents, since in the case of Hg TFE at higher concentrations of Ga(III) ions and In(III) ions in the solution a significant distortion of the anodic stripping peaks of both the analyzed elements takes place. Since the simultaneous presence of both the elements in the analyzed solution causes their mutual effects on the anodic peak heights, the method of standard additions at a constant concentration of a nonanalyzed element represents the most suitable method of their determination. The content of In(III) ions in the solution can be determined at Bi TFE (high linearity of the dependence of In peak height on In(III) concentration) and the content of Ga(III) ions at HgBi TFE for the same reasons. The comparison of actual contents of In (66.7 mass %) and Ga (33.3 mass %) in InGa alloy (prepared by mixing appropriate amounts of molten indium and gallium, dissolved in HNO_3 (60 %)) with the found ones (In content of 66.2 mass % (RSD = 5.2 %) and the content of Ga was 33.5 mass % (RSD = 0.9 %)) shows relatively high precision and accuracy of analysis achieved using the above-mentioned procedure.

Acknowledgements. This work was supported by the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences, Project No. 2/208422.

REFERENCES

1. Vasileva, L. N. and Vinogradova, E. N., *Zh. Anal. Khim.* 18, 454 (1963).
2. Moorhead, E. D. and Davis, P. H., *Anal. Chem.* 47, 622 (1975).
3. Zhao, X., Zhang, Z., Li, W., Jin, W., and Liu, W., *Anal. Chim. Acta* 318, 181 (1996).
4. Copeland, T. R., Osteryoung, R. A., and Skogerboe, R. K., *Anal. Chem.* 46, 2093 (1974).
5. Brett, Ch. M. A., Garcia, M. B. Q., and Lima, J. L. F. C., *Anal. Chim. Acta* 339, 167 (1997).
6. Varadharaj, A. and Prabhakara Rao, G., *J. Electroanal. Chem.* 138, 189 (1982).
7. Lukaszewski, Z., Pawlak, M. K., and Ciszew, A., *J. Electroanal. Chem.* 103, 217 (1979).
8. Florence, T. M., Batley, G. E., and Farrar, Y. J., *J. Electroanal. Chem. Interfacial Electrochem.* 56, 301 (1974).
9. Batley, G. E. and Florence, T. M., *J. Electroanal. Chem. Interfacial Electrochem.* 55, 23 (1974).
10. Wikiel, K. and Kublik, Z., *J. Electroanal. Chem.* 165, 71 (1984).
11. Wang, J., Lu, J., Kirgöz, V. A., Hocevar, S. B., and Ogorevc, B., *Anal. Chim. Acta* 434, 29 (2001).
12. Hansen, M., *Constitution of Binary Alloys*. McGraw-Hill, New York, 1958.