

Application of the catalytic properties of *N*-methylthiourea to the determination of In(III) at low levels by square wave voltammetry

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Abstract This article proposes a simple and fast method of In(III) determination in the presence of Cd(II) and Pb(II). The catalytic activity of *N*-methylthiourea was used in the In(III) electroreduction, which also had a slight effect on the electroreduction process of Cd(II) and Pb(II). By applying square wave voltammetry it was possible to determine $3 \times 10^{-7} \text{ mol dm}^{-3}$ In(III) in the presence of $5 \times 10^{-5} \text{ mol dm}^{-3}$ Cd(II) and $1 \times 10^{-4} \text{ mol dm}^{-3}$ Pb(II) in 5 mol dm^{-3} NaClO₄ at pH 2. The calibration curve for In(III) was linear from 3×10^{-7} to $5 \times 10^{-4} \text{ mol dm}^{-3}$. The relative standard deviation for In(III) determination was about 3.0%.

Keywords Indium(III) determination · *N*-Methylthiourea · Cadmium · Lead · Dropping mercury electrode · Square wave voltammetry

Introduction

The toxicity of indium means that monitoring its content in the natural environment is extremely important. It can be determined by spectroscopic and electrochemical methods. The electrochemical techniques are not only very sensitive but also inexpensive. During the determination of indium using electrochemical methods we should also consider the composition of the supporting electrolyte. In order to secure the irreversibility of In(III) electroreduction, the determination of indium should be carried out under strongly complexing conditions, even when using an

anodic stripping voltammetry method [1–4]. This is because the electroreduction of In(III) in solutions containing halide ions is more reversible which makes it possible to determine even up to $5 \times 10^{-10} \text{ mol dm}^{-3}$ In(III) [5–9], assuming the In(III) accumulates preliminarily on the electrode.

However In(III) determination does not come without problems, arising because of the presence of interferents such as Cd(II) and Pb(II), which appear in considerably higher concentrations than indium and the reduction potentials of these depolarizers differ from each other by several mV. In order to reduce the effect of these interferents, Neeb [3] applied a supporting electrolyte containing 0.5 mol dm^{-3} HBr + 2 mol dm^{-3} KI + ascorbic acid, that facilitated the determination of In(III) in the presence of $10^{-3} \text{ mol dm}^{-3}$ Cd(II). The peak of Pb(II) was separated from the peak of In(III) by addition of sodium tartrate. The interfering influence of Cd(II) can be reduced, if an electrode with gold contact is used [10], causing the formation of intermetallic compounds Cd–Au.

Florence et al. [11] determined In(III) by anodic stripping voltammetry using a hanging mercury drop electrode in different supporting electrolytes. In the acetate–bromide electrolyte they determined $1 \times 10^{-7} \text{ mol dm}^{-3}$ In(III) in the presence of $5 \times 10^{-6} \text{ mol dm}^{-3}$ Cd(II) and Pb(II). Charalambous et al. [12] used a bismuth film electrode for In(III) determination by square wave anodic stripping voltammetry in the presence of Cd(II) and Pb(II), which enabled determination of $10^{-7} \text{ mol dm}^{-3}$ In(III) in the presence of $5 \times 10^{-8} \text{ mol dm}^{-3}$ Cd(II) and Pb(II).

In our research we used the catalytic activity of *N*-methylthiourea (MTU) on the electroreduction of In(III) ions in chlorates(VII) [13]. We observed that in the presence of *N*-methylthiourea the height of the square wave voltammetry (SWV) peak of the In(III) electroreduction on

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mercury in solutions of chlorates(VII) increases substantially, but the heights of the Cd(II) and Pb(II) peaks increase to a lesser degree. Moreover, the peak of Cd(II) is shifted towards negative potentials, which enables the determination of In(III) in the presence of Cd(II) and Pb(II) without the need to use preconcentration.

Results and discussion

Addition of MTU to the In(III) ions in chlorate(VII) solution causes an increase in the reversibility of the electroreduction process. The catalytic activity of polarographically inactive organic substances in the electroreduction processes of metals forming amalgams was named the cap-pair effect [14]. It was found earlier that the electroreduction of In(III) is catalysed by thiourea [15], *N*-methylthiourea, *N,N*-dimethylthiourea [16], and *N*-allylthiourea [13], and that *N*-methylthiourea has the best catalytic activity. In the presence of MTU it is possible to obtain more reversible polarographic waves of In(III) electroreduction in chlorates(VII) along with much higher SWV peaks. With increasing MTU concentration the SWV peaks of In(III) electroreduction also increase (Fig. 1).

However, above the MTU concentration of 5×10^{-3} mol dm $^{-3}$ the increase of the SWV peak height of In(III) was considerably lower, hence this concentration was recognized as the optimum. Much higher increases of the SWV peak height of In(III) in the presence of MTU appear

in solutions of lower water activity. In the presence of 5×10^{-3} mol dm $^{-3}$ MTU SWV peaks of electroreduction of 1×10^{-6} In(III) in 1 mol dm $^{-3}$ NaClO $_4$ and 3×10^{-7} mol dm $^{-3}$ In(III) in 5 mol dm $^{-3}$ NaClO $_4$ can be obtained (Fig. 2).

The calibration curves of In(III) in 1 and 5 mol dm $^{-3}$ NaClO $_4$ at pH 2 in the presence of 5×10^{-3} mol dm $^{-3}$ MTU are linear in the range of concentrations of In(III) from 1×10^{-6} to 1×10^{-4} mol dm $^{-3}$ in 1 mol dm $^{-3}$ NaClO $_4$ and from 3×10^{-7} to 5×10^{-4} mol dm $^{-3}$ in 5 mol dm $^{-3}$ NaClO $_4$. At higher concentrations of In(III) there are substantial deviations from linearity.

The determination of In(III) was also carried out in the presence of 5×10^{-5} mol dm $^{-3}$ Cd(II) and 1×10^{-4} mol dm $^{-3}$ Pb(II). In the solutions which did not contain MTU the electroreduction peak for In(III) was not visible for In(III) concentrations below 5×10^{-4} mol dm $^{-3}$ (Fig. 3, dotted line).

After adding 5×10^{-3} mol dm $^{-3}$ of MTU the peak in the solution containing 3×10^{-5} mol dm $^{-3}$ In(III) in 1 mol dm $^{-3}$ NaClO $_4$ at pH 2 and 6×10^{-6} mol dm $^{-3}$ In(III) in 5 mol dm $^{-3}$ NaClO $_4$ at pH 2 was obtained. The presence of MTU in the solution increased the minimal heights of the SWV peak of Pb(II) electroreduction, the potential of the peaks however did not change. The influence of the MTU on the height of the SWV peak of the Cd(II) electroreduction was slightly higher. We observed a 40% increase in the height of the SWV peak of Cd(II), this peak shifted about 43 mV towards negative potentials.

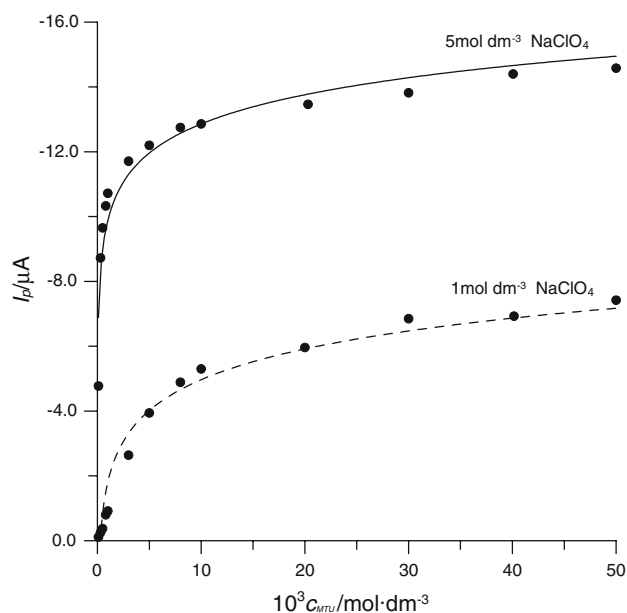


Fig. 1 The dependence of 5×10^{-4} mol dm $^{-3}$ In(III) SWV peak current (I_p) on the concentration of *N*-methylthiourea (C_{MTU}) in 1 mol dm $^{-3}$ NaClO $_4$ at pH 2 (dashed lines) and 5 mol dm $^{-3}$ NaClO $_4$ at pH 2 (continuous lines)

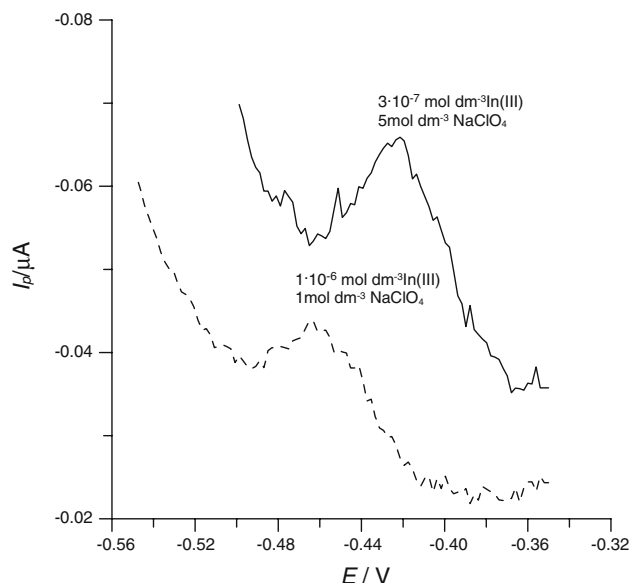


Fig. 2 SWV peaks of 1×10^{-6} mol dm $^{-3}$ In(III) electroreduction in 1 mol dm $^{-3}$ NaClO $_4$ at pH 2 (dashed lines) and 3×10^{-7} mol dm $^{-3}$ In(III) in 5 mol dm $^{-3}$ NaClO $_4$ at pH 2 (continuous lines) in the presence of 5×10^{-3} mol dm $^{-3}$ *N*-methylthiourea (E —the potential peak)

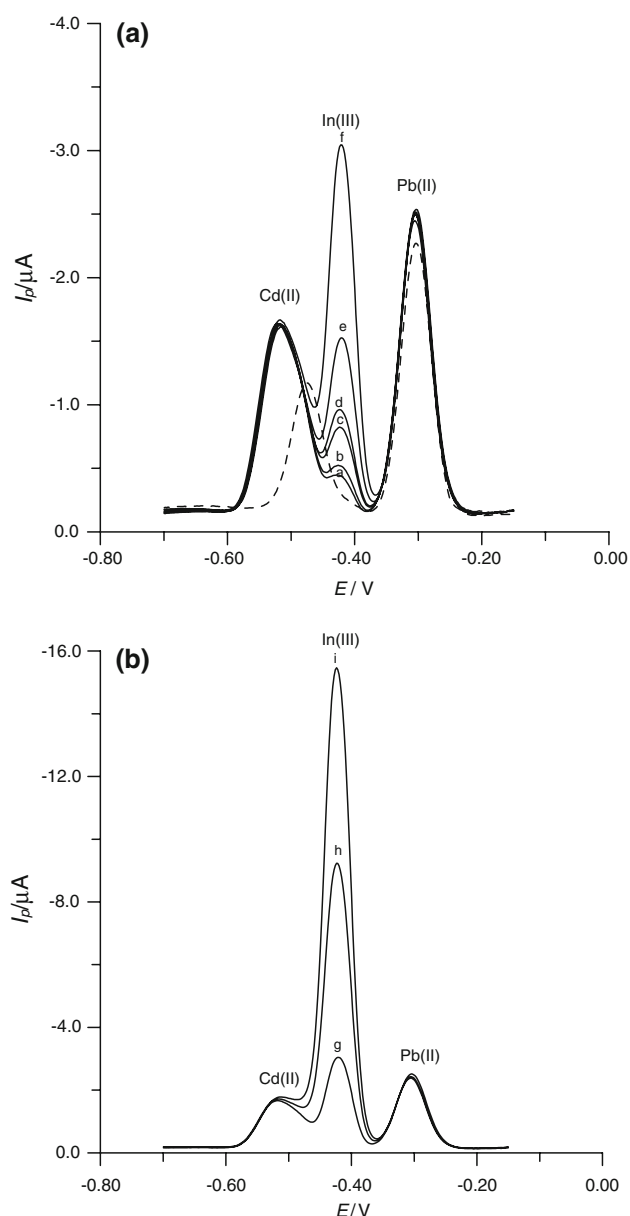


Fig. 3 **a, b** SWV peaks of In(III) electroreduction in 5 mol dm⁻³ NaClO₄ at pH 2 in the presence of 5 × 10⁻³ mol dm⁻³ *N*-methylthiourea + 1 × 10⁻⁴ mol dm⁻³ Pb(II) + 5 × 10⁻⁵ mol dm⁻³ Cd(II). Concentration of In(III) in mol dm⁻³: 6 × 10⁻⁶ (a), 1 × 10⁻⁵, (b), 2 × 10⁻⁵, (c), 3 × 10⁻⁵, (d), 5 × 10⁻⁵ (e), 8 × 10⁻⁵, (f), 1 × 10⁻⁴, (g), 3 × 10⁻⁴, (h), 5 × 10⁻⁴, (i) The dotted line is the SWV peak of a solution of 8 × 10⁻⁵ mol dm⁻³ In(III) in 5 mol dm⁻³ NaClO₄ at pH 2 + 1 × 10⁻⁴ mol dm⁻³ Pb(II) + 5 × 10⁻⁵ mol dm⁻³ Cd(II) without *N*-methylthiourea

Although this shift of potential of the Cd(II) peak does not depend on the MTU concentration, it creates larger possibilities for In(III) determination in the presence of Cd(II). It is worth adding that the potential of the In(III) peak did not change after adding MTU to the solution (Fig. 3).

The calibration curves of In(III) in 1 and 5 mol dm⁻³ NaClO₄ at pH 2 containing 5 × 10⁻³ mol dm⁻³ MTU and

5 × 10⁻⁵ mol dm⁻³ Cd(II) and 1 × 10⁻⁴ mol dm⁻³ Pb(II) were made. The dependences were linear in the range of concentrations of In(III) from 1 × 10⁻⁶ to 7 × 10⁻⁴ mol dm⁻³ in 1 mol dm⁻³ NaClO₄ and from 3 × 10⁻⁷ to 5 × 10⁻⁴ mol dm⁻³ in 5 mol dm⁻³ NaClO₄ and obeyed the equations: $y = -1.9x - 0.29$ and $y = -3.0x - 0.11$, respectively. The applied method was evaluated by comparison of the declared concentration of In(III) with the concentration obtained from a calibration curve. The relative standard deviation for In(III) determination in 1 mol dm⁻³ NaClO₄ at an In(III) concentration of 1 × 10⁻⁵ mol dm⁻³ was 2.8% ($n = 5$). In 5 mol dm⁻³ NaClO₄ the relative standard deviation for In(III) determination at a concentration of 8 × 10⁻⁶ mol dm⁻³ was 3.0%.

Conclusion

Addition of *N*-methylthiourea to a chlorate(VII) solution at pH 2 causes a substantial increase in the reversibility of In(III) ion electroreduction, which could be explained by the large increase of the height of the SWV peaks and the limit of In(III) determination at about 10⁻⁷ mol dm⁻³. It was found that the determination of In(III) can also be carried out in the presence of Cd(II) and Pb(II), because *N*-methylthiourea only slightly affects the height of the SWV peaks of these interferences. Moreover the electroreduction peak of Cd(II) is shifted towards electronegative potentials, which also facilitates determination of In(III). This method is simple and fast in comparison to methods requiring preconcentration of an analyte, precipitation, or complexing of interfering ions.

Experimental

The measurements were performed using Autolab (Eco Chemie, The Netherlands). The working electrodes were a hanging mercury drop electrode made by MTM Poland, saturated Ag/AgCl (NaCl) as reference electrode, and a Pt wire as counter electrode. The reference electrode was fitted with a Luggin capillary probe. The capillary was filled with the cell solution.

The solutions were prepared from fresh, triply distilled, water and analytical grade chemicals. A supporting electrolyte of 1 or 5 mol dm⁻³ NaClO₄ at pH 2 was used. The standard solution of In(III) was prepared from In(NO₃)₃·5H₂O (Aldrich) by dissolution in concentrated HClO₄ and then dilution with supporting electrolyte. The solutions of Cd(II) and Pb(II) were prepared from Cd(NO₃)₂·4H₂O (Fluka) and Pb(NO₃)₂ (POCh Poland). *N*-methylthiourea (MTU) was obtained from Fluka. Only

freshly prepared solutions of MTU were used. The solutions were deaerated using a purge of nitrogen that was first passed through a vanadous sulfate solution and then pre-saturated with the investigated solution. The measurements were carried out at room temperature.

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