

## ADSORPTIVE STRIPPING VOLTAMMETRIC DETERMINATION OF BUTANTHIOL AND CYCLOHEXANTHIOL

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Received December 30th, 1983

1-Butanthiol and cyclohexanthiol is determined by cathodic stripping voltammetry with adsorptive accumulation of the formed mercury salts of the thiols on the surface of the hanging mercury drop electrode. Butanthiol can be determined in the concentration range from  $9.0 \mu\text{g l}^{-1}$  to  $1.8 \text{ mg l}^{-1}$ , cyclohexanthiol in the range from  $90 \mu\text{g l}^{-1}$  to  $2.5 \text{ mg l}^{-1}$ . The method can be applied for the analysis of polluted air, after trapping the thiol in ammonium hydroxide-methyl alcohol mixture. Sulphides do not interfere with the determination.

Sulphur containing organic compounds play an important role in living systems and analytical methods for their determinations are therefore necessary. Electrochemical determinations of compounds containing mercapto group — thiols — are principally based on the formation of insoluble salts of these compounds with mercury. An anodic wave corresponding to the mentioned reaction is measured if polarography is applied for the determination — an example is the determination of non protein —SH group<sup>1</sup>. The amperometric titration methods with mercury containing titrant, where mercury electrodes are commonly applied<sup>2</sup> represent another possibility of thiols determination. Interest has been also paid to the methods based on the measurement of a catalytic wave which was observed when a compound with —SH group is added to an ammoniacal solution of cobalt salt<sup>3</sup>.

Because in many cases the formed mercury salt is adsorbed on the surface of the mercury electrode, highly sensitive determinations based on cathodic stripping voltammetry with adsorption accumulation of the formed mercury salt can be realized. In this work are presented the results obtained in the study of the possibilities of a cathodic stripping voltammetric determination of 1-butanthiol and cyclohexanthiol with adsorptive accumulation on hanging mercury drop electrode.

### EXPERIMENTAL

#### Apparatus

Polarographic analyzer PA-4 (Laboratorní přístroje, Prague) was used in three electrode configurations for recording of d.c., differential pulse polarographic (DPP), normal pulse polarographic (NPP) and fast scan DPP (FSDPP) curves. A static mercury drop electrode SMDE-1 (Laboratorní přístroje, Prague) served as working electrode in connection with Ag/AgCl reference

electrode and platinum auxiliary electrode. Dissolved oxygen was removed from the test solutions by prepurified nitrogen.

#### Reagents

$10^{-3} \text{ mol l}^{-1}$  solutions of 1-butanthiol ( $\text{C}_4\text{H}_{10}\text{S}$ ) and cyclohexanthiol ( $\text{C}_6\text{H}_{12}\text{S}$ ) were prepared by dissolving the corresponding chemicals in methanol. These reagents were obtained in pure form from the Department of organic chemistry, Charles University, Prague. All used solutions were prepared from reagent grade chemicals; twice-distilled water (quartz apparatus) was used throughout.

#### Procedure for Cathodic Stripping Voltammetry (CSV) with Adsorptive Accumulation

The hanging mercury drop electrode (realized with the use of the SMDE) is kept at the accumulation potential in a stirred solution (mechanical stirring with constant rate). During stirring the fresh mercury drop is dislodged on the static mercury drop electrode assembly and from that instant the accumulation time is counted. After switching off the stirrer, the solution is allowed to rest for another 15 s. The potential is then scanned in cathodic direction with preselected scan rate.

The sequence of all described operations (with preselected time and potential values) was performed automatically using the automatics involved in the analyzer PA-4.

## RESULTS

### *Polarographic and Voltammetric Behaviour of Butanthiol and Cyclohexanthiol*

Preliminary experiments have shown that well developed DPP peaks of butanthiol (BT) and cyclohexanthiol (CHT) were obtained when HMDE was used as the working electrode in alkaline media (0.2M-KOH or 0.2M-KOH containing 20% vol. methyl-alcohol). In d.c. polarographic measurements BT yielded an anodic double wave with the half-wave potentials  $-0.55$  and  $-0.65 \text{ V}$  (Ag/AgCl) when 0.2M-KOH was applied as supporting electrolyte. The corresponding current was of adsorption nature; this follows from the NPP measurement where a wave with a sharp maximum at the potential  $-0.65 \text{ V}$  was recorded. This corresponds with the finding that the d.c. limiting current did not increase linearly with increasing BT concentration (above  $10^{-3} \text{ mol l}^{-1}$  BT). Under identical conditions DPP yielded an unsymmetrical peak with the peak potential ( $E_p$ ) value  $-0.58 \text{ V}$ . If in these measurements the DME was replaced by the HMDE and DPP peak was obtained with the peak potential value equal to  $-0.65 \text{ V}$  and the height of this peak increased 50 times in comparison with that obtained with DME.

As expected the peak current increased with prolonged accumulation time — the time interval during which the HMDE was kept at the accumulation potential  $E_{acc}$  — the potential more positive than was the value  $E_p$ . The dependence of the peak current on accumulation time has the nature of an adsorption isotherm and is

shown in Fig. 1. The optimum value of the accumulation potential was determined from the dependence of the  $E_{acc}$  values on the peak current. The maximum peak current was obtained in the accumulation potential range from  $-0.10$  to  $-0.30$  V; when more negative accumulation potential values were applied the peak current gradually decreased.

The phenomena described above are observed under the conditions when the concentration interval between  $1 \cdot 10^{-7}$  and  $1 \cdot 10^{-5} \text{ mol l}^{-1}$ ; at higher BT concentration two or three peaks appeared on the voltammogram with the  $E_p$  values  $-0.65$ ,  $-0.73$  and  $-0.78$  V. Under such conditions the peak current did not increase with prolonged accumulation time. It can be concluded that with high BT concentration the surface area of the electrode is completely covered with the adsorbed species and the electrode process becomes more complex.

The described results verify that BT is accumulated on the surface of the HMDE by adsorption and determined in the subsequent cathodic polarization scan. Using the accepted nomenclature the method involved is a cathodic stripping voltammetry (CSV) with adsorptive accumulation<sup>4</sup>. Because the mercury salt of BT is formed in positive potential region, this salt is adsorbed on the electrode surface, similarly as in the case of CSV determination of thiourea and its derivatives<sup>5</sup>.

The dependence of the peak current on BT concentration was found linear in the concentration range from  $1 \cdot 10^{-7}$  to  $2 \cdot 10^{-5} \text{ mol l}^{-1}$  BT ( $9.0 \mu\text{g l}^{-1}$  to  $1.8 \text{ mg l}^{-1}$ ) with the slope corresponding to  $11 \text{ nA per } 10 \mu\text{g BT}$ . In these measurements short accumulation time —  $10 \text{ s}$  — was applied and above the concentration  $5 \cdot 10^{-6} \text{ mol l}^{-1}$  BT the measurement was carried out with zero accumulation time.

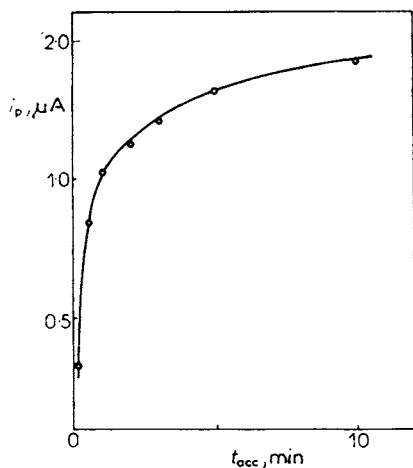


FIG. 1

Dependence of peak current on accumulation time in CSV of butanthiol.  $9 \cdot 10^{-6} \text{ mol l}^{-1}$  BT in  $0.1 \text{ M-KOH}$  containing  $20\% \text{ v. methyl alcohol}$ ; accumulation potential  $-0.30 \text{ V}$ , FSDPP, HMDE (SMDE 1), polarization rate  $20 \text{ mV s}^{-1}$

Similar results were obtained with  $\text{NH}_4\text{OH}$  + methyl alcohol (20% vol.) as the base electrolyte with the only difference that the peak potential of BT was slightly shifted to more negative values ( $-0.68\text{ V}$ ). It was also established that the peak current values were practically unaffected by varying the amount of methyl alcohol in the base electrolyte in the range from 5 to 20% vol.

#### *Influence of Sulphide Ions on CSV of Butanthiol*

It can be expected that the polarographic and voltammetric behaviour of sulphide ions will be similar to that of BT. Sulphide ions yielded an anodic polarographic (d.c.) wave with the half-wave potential  $-0.76\text{ V}$  (S.C.E.) in  $0.1\text{ M-NaOH}$  (ref.<sup>6</sup>). If, on the other hand, the HMDE was used in this determination, sulphide ions yielded a DPP peak with the  $E_p$  value  $-0.82\text{ V}$  (Ag/AgCl) in  $0.1\text{ M-NH}_4\text{OH}$  with 20% vol. of methyl alcohol. These results show that under given conditions BT and sodium sulphide can be determined simultaneously (Fig. 2). If the sample solution contained a large excess of sulphide ions, these could be masked by the addition of lead(II) ions (Fig. 2). The BT peak current was found to decrease by approx. 15% in the presence of a hundred times excess of lead(II) ions and thus the sensitivity of determination is only slightly affected by the presence of the masking reagent.

#### *Cathodic Stripping Determination of Cyclohexanthiol*

The experiments showed that the voltammetric behaviour of cyclohexanthiol (CHT) was very similar to that of BT. Well developed DPP peaks or d.c. polarographic waves were obtained in alkaline media ( $0.1\text{ M-NH}_4\text{OH}$  or  $0.1\text{ M-KOH}$ ). The cathodic

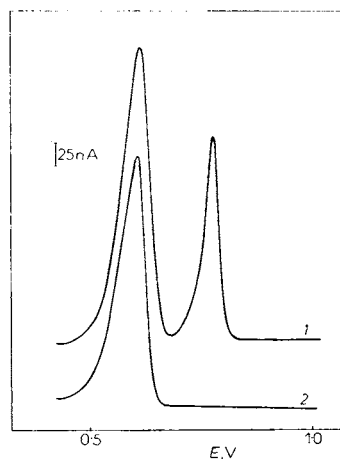


FIG. 2

CSV curves of butanthiol and sodium sulphide.  $1\ 5 \cdot 10^{-6}\text{ mol l}^{-1}$  BT and  $8 \cdot 10^{-6}\text{ mol l}^{-1}$   $\text{Na}_2\text{S}$  in  $0.1\text{ M-NH}_4\text{OH}$  containing 10% v. methyl alcohol; accumulation potential  $0.30\text{ V}$ , accumulation time  $10\text{ s}$ , FSDPP, HMDE (SMDE 1), polarization rate  $20\text{ mV s}^{-1}$ . 2 after addition of  $100\ \mu\text{l}$   $0.1\text{ M-Pb(NO}_3)_2$

stripping of CHT was, however, influenced by the presence of methyl alcohol in the base electrolyte, the corresponding current did not change with varied CHT concentration or with varied accumulation time. Well developed peaks of CHT (peak potential  $-0.70$  V) were on the other hand recorded in  $1\text{M-KOH}$ . The peak current vs CHT concentration dependence was found linear in the concentration range from  $8 \cdot 10^{-7} \text{ mol l}^{-1}$  to  $1.6 \cdot 10^{-5} \text{ mol l}^{-1}$  with the slope of the calibration line corresponding to  $6 \text{ nA per } 100 \mu\text{g CHT}$ . These data were obtained under identical conditions under which the CSV of BT was realized. It was verified experimentally that the dependences of the CSV peak current on the accumulation time and on the accumulation potential had a similar course as those for BT.

From the values of the peak potentials of BT and CHT it follows that the simultaneous determination of both thiols is not possible using CSV adsorptive accumulation.

#### *Influence of BT and CHT on ASV of Copper*

It has been described that the presence of some  $-\text{SH}$  group containing compounds increased the sensitivity of the ASV determination of copper<sup>7</sup>. In the presence of such compounds a new, sharp peak appeared at more positive potential than corresponded to the copper dissolution in ASV of copper carried out in neutral or slightly acidic media. This effect is caused by the formation of mercury and copper complexes with the analyzed compound and their adsorption on the surface of the mercury electrode. The second dissolution peak of copper was observed also in the ASV determination of copper carried out in the presence of BT or CHT in neutral medium. The new peak is in this case caused by the same phenomena as described by the Japanese authors<sup>7</sup>. The new peak appeared on the voltammogram only at higher copper concentration and thus no increase of the copper ASV determination could be reached as in the case of *e.g.* cysteine.

#### *Analytical Application*

The results presented above were applied for the determination of BT in the air. The air artificially contaminated with BT was trapped into 1 : 1 mixture of  $0.1\text{M-NH}_4\text{OH}$  and methyl alcohol and determined after dilution with ammonium hydroxide.

The air to be analyzed was passed through three impingers (volume  $25 \text{ ml}$ ) each containing  $10 \text{ ml}$  of the ammonium hydroxide-methyl alcohol mixture at a flow rate  $500 \text{ ml}$  for  $30-60 \text{ min}$ . The analysis of the mixtures corresponding to each separate impinger showed that no BT was trapped in the third impinger after one hour passing the contaminated air through the series of three impingers. For the analysis of the air samples the content of the first two impingers was transferred into a  $50 \text{ ml}$  volumetric flask and diluted to the mark with  $0.1\text{M-NH}_4\text{OH}$ . This solution was used for the adsorptive stripping voltammetric determination of BT in the measured amount of the air.

Because sodium sulphide vapors are trapped in the used methanolic mixture, BT can be determined simultaneously with sulphide or in samples containing large amounts of sulphide when the masking with lead(II) is used.

Recommended parameters for the adsorptive stripping voltammetry of BT: Accumulation potential  $-0.20$  V (Ag/AgCl), accumulation time  $0-60$  s with stirring, rest period  $15$  s, polarization rate  $20$  mV s $^{-1}$  in the range from  $-0.20$  to  $-1.00$  V (Ag/AgCl), measurement mode fast scan differential pulse polarography with pulse amplitude  $-10$  mV to  $-50$  mV. Results are evaluated by standard additions.

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Translated by the author (M. K.).