

**POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF 4,4'-BIS[(4-DIETHANOLAMINO-6-(2,5-DISULFOPHENYLAMINO)-1,3,5-TRIAZIN-2-YL)AMINO]STILBENE-2,2'-DISULFONIC ACID**Jiri BAREK<sup>a1</sup>, Roman HRNCIR<sup>b</sup>, Josino C. MOREIRA<sup>c</sup> and Jiri ZIMA<sup>a2</sup><sup>a</sup> UNESCO Laboratory of Environmental Electrochemistry, Department of Analytical Chemistry, Charles University, 128 40 Prague 2, Czech Republic; e-mail: <sup>1</sup> Barek@prfdec.natur.cuni.cz,<sup>2</sup> Zima@prfdec.natur.cuni.cz<sup>b</sup> Severochema Cooperative, 461 71 Liberec, Czech Republic<sup>c</sup> CESTEH/ENSP/FIOCRUZ, Rua Leopoldo Bulhoes 1480, Manguinhos, 210 41-210 Rio de Janeiro, Brazil; e-mail: Josino@DCC001.CICT.FIOCRUZ.BR

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The polarographic and voltammetric behaviour was studied for 4,4'-bis[(4-diethanolamino-6-(2,5-disulfophenylamino)-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid, which is the basis of many commercial optical whitening agents. The optimum conditions were found for quantitation of this substance in tetraethylammonium bromide solutions in dimethylformamide containing 5% (v/v) water using TAST polarography, differential pulse polarography, linear sweep voltammetry at a hanging mercury drop electrode, and differential pulse voltammetry at a hanging mercury drop electrode over the concentration regions of 100–500, 10–500, 10–500, and 1–100  $\mu\text{mol l}^{-1}$ , respectively. The practical applicability of the new analytical methods to the determination of the substance in technical products was verified.

**Key words:** Polarography; Voltammetry; Optical brightening agents; 4,4'-Bis[(4-diethanolamino-6-(2,5-disulfophenylamino)-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid.

Optical whitening agents are among organic pollutants which are discharged into wastewaters from industrial processes. Substituted derivatives of 4,4'-diaminostilbenedisulfonic acid constitute an important group within this class of substances. Although the substances are usually not assumed to pose a health hazard or environmental hazard<sup>1,2</sup>, their monitoring is of importance in view of their possible mutagenity, although their carcinogenic effects have not been demonstrated<sup>3</sup>. An overview of titrimetric, spectrophotometric, fluorometric and separation methods applicable to the quantitation of various derivatives of 4,4'-diaminostilbenedisulfonic acid was presented previously<sup>4</sup>. Their polarographic determination has not attracted much interest so far, due to the difficult polarographic reducibility of substances of this type<sup>4,5</sup>. Some derivatives of 4,4'-bis(triazinylamino)stilbene-2,2'-disulfonic acid have been studied by AC polarography and oscillopolarography<sup>6–9</sup>. Many papers were devoted to the polarographic reduction of the C=C double bond in stilbene and its derivatives<sup>10–20</sup>, largely in dioxane,

dimethylformamide or acetonitrile solutions containing 0 to 25% water in the presence of tetrabutylammonium iodide or tetraethylammonium bromide. Tetrahydrofuran<sup>11</sup> and butanol<sup>12</sup> or ethanol<sup>13</sup> in mixtures with water have also been tested. The various stilbene derivatives give polarographic waves with  $E_{1/2}$  from  $-2.1$  to  $-2.8$  V vs SCE in dependence on the composition of the medium. The mechanism of reduction of the C=C bond in stilbene derivatives was the concern of refs<sup>14-16</sup> and has been discussed in our previous paper<sup>4</sup>.

The present work deals with the polarographic behaviour of 4,4'-bis[(4-diethanolamino-6-(2,5-disulfophenylamino)-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid (BDTSDA, see formula **1** in Scheme 1), which is the basis of many commercial optical whitening agents such as Bayer's Blankophor BSU or the Czech product Rylux BSU. The aim of this work was to develop methods for the determination of low concentrations of this organic pollutant by modern polarographic and voltammetric techniques, particularly by differential pulse polarography (DPP) using the conventional dropping mercury electrode (DME) and by differential pulse voltammetry (DPV) using the hanging mercury drop electrode (HMDE). Based on experience gained during the investigation of the structurally related 4,4'-bis[(4-phenylamino-6-methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid<sup>4</sup> and 4,4'-bis[(4-phenylamino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid<sup>5</sup>, a solution of tetraethylammonium bromide in dimethylformamide containing 5% (v/v) water was chosen as the electrolyte because this system allows sufficiently negative potentials to be reached, as required for the polarographic reduction of the C=C bond in the stilbene system.

## EXPERIMENTAL

### Reagents

BDTSDA, hexasodium salt ( $C_{40}H_{38}N_{12}Na_6O_{22}S_6$ , CAS Name: 2,2'-(1,2-ethenediyl)bis[5-[(4-(bis(2-hydroxyethyl)amino)-6-((3,6-disulfophenyl)amino)-1,3,5-triazin-2-yl)amino]benzenesulfonic acid, hexasodium salt; CAS Registry Number 41098-56-0) was obtained by double recrystallization of the technical product Blankophor BSU (Bayer, Leverkusen, Germany) from a water-methanol 1 : 1 mixture. The stock solution of this compound in dimethylformamide (DMF) at a concentration of  $1 \text{ mmol l}^{-1}$  was prepared by dissolving 1.3691 g of the substance in the solvent and diluting to 1 l. More dilute solutions were prepared by dilution of this stock solution with DMF. The purity and active content of the preparations were checked by oxidimetric and precipitation titrations, thin layer chromatography and spectrophotometry (see below). In order to prevent *cis-trans* isomerization, the solutions were prepared, diluted and stored in dark and the measurements were performed using brown glass vessels.

Dimethylformamide (pure, Lachema Brno, Czech Republic) was distilled several times in the presence of potassium hydroxide prior to use<sup>21</sup>. Tetraethylammonium bromide (pure, Lachema Brno, Czech Republic) was recrystallized from the water-methanol 1 : 1 system.

Septonex ([1-(ethoxycarbonyl)pentadecyl]trimethylammonium bromide) used for the titrimetric determination was of purity complying with PhBS 4 (Slovakofarma, Hlohovec, Slovak Republic).

Water was redistilled in a quartz still.

The technical whitening agent Rylux BSU was a product of VCHZ Synthesia, Pardubice, Czech Republic.

The other chemicals used were of reagent grade purity (Lachema Brno, Czech Republic).

#### Apparatus

A PA4 polarographic analyzer interfaced to an XY 4105 recorder (both Laboratorni pristroje, Prague, Czech Republic) was employed. The working electrode was either a conventional DME (for fast polarography and DPP) or an SMDE 1 static mercury drop electrode (Laboratorni pristroje, Prague, Czech Republic) in the HMDE mode; the reference electrode was a saturated silver chloride electrode, which was interfaced to the analyte solution through a salt bridge containing  $0.1 \text{ mol l}^{-1}$  tetraethylammonium bromide in DMF. The three-electrode connection involving a platinum sheet electrode was applied. The potentials measured were converted relative to the standard calomel electrode.

The DME reservoir height was 25 cm. The capillary was selected to give a relatively long drop time, viz. 8.91 s in  $0.1 \text{ mol l}^{-1}$  KCl at 0 V, the mercury mass flow rate was  $0.38 \text{ mg s}^{-1}$ . The inner diameter of the HMDE capillary was 0.138 mm, and the maximum drop size was employed (the valve opening period of 160 ms).

The potential sweep rate was  $5 \text{ mV s}^{-1}$  for fast polarography and DPP, and  $20 \text{ mV s}^{-1}$  for LSV and DPV; the electronically controlled drop time was 1 s and the pulse height was  $-50 \text{ mV}$  (DPP) or  $-25 \text{ mV}$  (DPV).

Oxygen was removed from the solutions by nitrogen purging, using nitrogen which had been passed through a solution of chromium(II) ions in dilute (1 : 1) HCl over a zinc amalgam. A bubbler containing the same supporting electrolyte as the measuring cell was inserted before the cell.

Absorption spectra were scanned on a Pye Unicam PU 8800 UV/VIS spectrophotometer (Philips, Cambridge, U.K.) using quartz cells 1 and 2 cm optical pathlength.

Oxidimetric potentiometric titrations were performed by using an MM 6 electromagnetic stirrer (PM, Poland) and an OP 208/1 pH-meter (Radelkis, Budapest, Hungary) equipped with a platinum wire indicator electrode and a saturated calomel reference electrode. Precipitation titrations were carried out on a Spekol 11 photometer fitted with a Ti titration adapter (Zeiss, Jena, Germany); cell volume 30 ml, wavelength 700 nm.

Thin layer chromatography was performed on Silufol UV 254 plates (Kavalier, Votice, Czech Republic) using a commercial chromatographic kit.

An M 415 centrifuge (Chirana, Czech Republic) and a Model 350 rotary vacuum evaporator (Unipan, Poland) were employed during the purification and separation processes.

All measurements were performed at room temperature.

#### Procedures

For the polarographic and voltammetric measurements, a volume of 1 ml of tetraethylammonium bromide solution in DMF ( $c = 0.1 \text{ mol l}^{-1}$ ) was pipetted into a 10 ml volumetric flask, 0.5 ml of redistilled water and the appropriate amount of BDTSDA solution in DMF were added, and the system was diluted to volume with DMF. The polarographic or voltammetric curve was recorded after a 10 min nitrogen purging. Calibration curves were measured in triplicate and processed by linear regression applying the least squares method. The limit of determination  $L_Q$  was calculated as the tenfold standard deviation of 7 analyte determinations at the concentration corresponding to the lowest point of the calibration straight line<sup>22</sup>.

When checking the purity of the substance by TLC,  $10 \mu\text{l}$  of a  $1 \cdot 10^{-3} \text{ mol l}^{-1}$  solution of BDTSDA in DMF were applied to the start, and the solvent was removed by evaporation with a

stream of warm air. The ascending chromatographic mode was used. All work, from the solution preparation to the drying of the developed chromatogram, was carried out in a dark room under the light of a red lamp and the elution was conducted in a closed tank. The detection consisted in a short illumination with an UV lamp. The following mobile phases were employed: methanol–chloroform–ammonia 7 : 8 : 2 ( $R_F = 0.02$ ), isopropyl alcohol–ethyl acetate–water–ammonia 46 : 30 : 23 : 1 ( $R_F = 0.18$ ), methanol–ethyl acetate 2 : 1 ( $R_F = 0.23$ ), methanol–6 M HCl 5 : 1 ( $R_F = 0.65$ ), and methanol–6 M HCl–chloroform 35 : 5 : 7 ( $R_F = 0.82$ ).

The oxidimetric determination of BDTSDA in the substances examined was based on the method<sup>23</sup> consisting in the oxidation of the stilbene double bond with permanganate giving rise to two molecules of the corresponding aldehyde. The procedure was as in ref.<sup>4</sup>; 1 ml of  $\text{KMnO}_4$  solution at  $c = 0.033 \text{ mol l}^{-1}$  corresponded to 0.0343 g of BDTSDA.

Precipitation titrations of BDTSDA employed Septonex as the titrant: 1 molecule of analyte reacted with 6 molecules of Septonex<sup>24</sup>. The procedure was as in ref.<sup>4</sup>. The end point was detected turbidimetrically at a wavelength of 700 nm, chosen with respect to the own fluorescence and absorption of BDTSDA. One ml of  $0.0065 \text{ mol l}^{-1}$  Septonex corresponded to 1.483 mg of BDTSDA.

The following procedure was applied to the polarographic determination of BDTSDA in the technical products Blankophor BSU and Rylux BSU. Approximately 0.1 g of sample, precisely weighed, was dissolved in DMF in a 50 ml volumetric flask and diluted to volume with this solvent. An 1 ml aliquot was pipetted into a 10 ml volumetric flask, 1 ml of tetraethylammonium bromide solution in DMF ( $c = 10 \text{ mmol l}^{-1}$ ) and 0.5 ml of redistilled water were added, and the whole was diluted to volume with DMF. Oxygen was removed by nitrogen purging, and the cast or DP polarogram was recorded. The analyte content was read from a calibration graph based on the wave or peak height.

## RESULTS AND DISCUSSION

### *Checking the Purity of BDTSDA and the Stability of Its Stock Solutions*

The BDTSDA content of the recrystallized substance was checked as described in the Experimental. Oxidimetric and precipitation titrations gave 98.9% and 98.1% contents, respectively. Thin layer chromatography gave evidence that the substance involved a single compound. The UV spectrum of the stock solution of BDTSDA in DMF ( $c = 0.02 \text{ mmol l}^{-1}$ ) is shown in Fig. 1. Since compounds of this type are subject to *cis-trans*

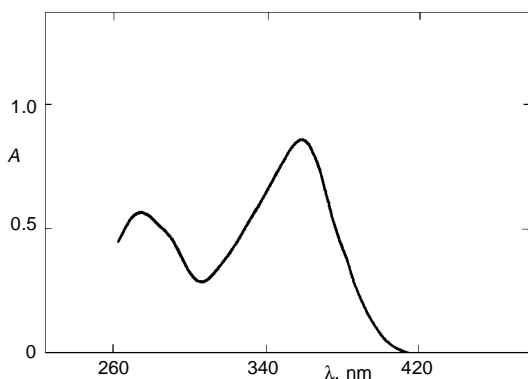


FIG. 1  
UV absorption spectrum of BDTSDA in DMF;  $c = 0.02 \text{ mmol l}^{-1}$ , optical path-length 1 cm

isomerization, their absorption spectra have to be measured immediately after solution preparation in dark, and/or their absorbance in the isosbestic point, which is unaffected by isomerization, is taken into account. The absorption maxima of BDTSDA in DMF lie at 272 and 359 nm, and its isosbestic point lies at 330 nm. The molar absorptivities at 359 and 330 nm were found to be  $4.62 \cdot 10^4$  and  $2.97 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ , respectively, in agreement with published data<sup>1</sup>. As evidenced by DPP at a DME, the concentration of the stock solution of BDTSDA in DMF at  $c = 1 \text{ mmol l}^{-1}$  does not decrease with time more than 1% in 10 days and 2% in 30 days.

### Tast Polarography and Differential Pulse Polarography Using a Dropping Mercury Electrode

Based on our previous experience<sup>4,5</sup>, DMF containing 5% (v/v) water was chosen as the solvent, allowing sufficiently negative potentials (up to  $-2.7 \text{ V}$  vs SCE) to be attained using tetraethylammonium bromide as the supporting electrolyte. DMF free of water proved to be a poorer solvent: the records were frequently spoiled due to the irregular dropping of mercury at potentials more negative than  $-2 \text{ V}$  vs SCE. In this system, BDTSDA ( $c = 0.3 \text{ mmol l}^{-1}$ ) gives two tast polarographic waves or DP polarographic peaks (Fig. 2). The first wave or peak, with the half-wave potential  $E_{1/2} = -2.02 \text{ V}$  or peak potential  $E_p = -1.99 \text{ V}$ , apparently corresponds to the reduction of sodium ions. The DC polarographic wave height is directly proportional to the squared root of the mercury reservoir height and to the concentration of sodium ions, as demonstrated by addition of sodium chloride. This wave or peak is practically unusable because real samples always contain some inorganic salts, affecting its height.

The other wave or peak, with  $E_{1/2} = -2.29 \text{ V}$  and  $E_p = -2.28 \text{ V}$ , is apparently due to the reduction of the double bond of the stilbene system. No shift in the  $E_{1/2}$  or  $E_p$  position that would indicate *cis-trans* isomerization was observed within 60 min. The term  $k = I_{\text{lim}}/(m^{2/3} t^{1/6})$ , where  $I_{\text{lim}}$  is the limiting current of this wave as obtained by tast polarography,  $m$  is the mercury mass flow rate, and  $t$  is the electronically controlled

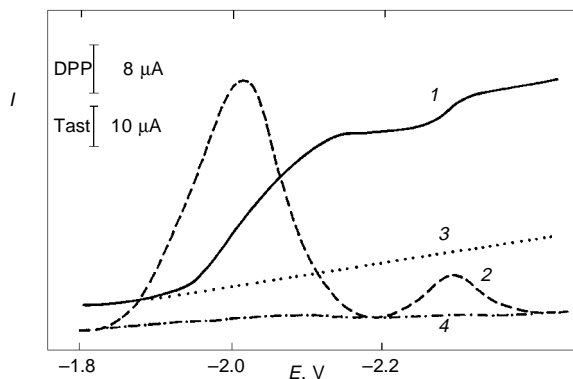
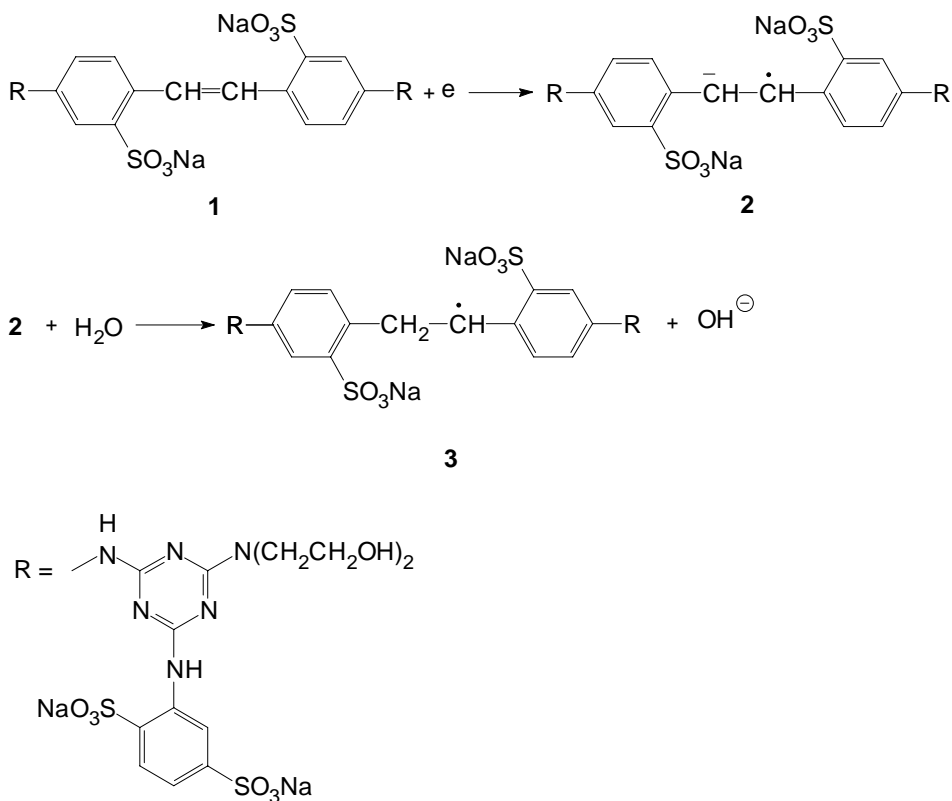


FIG. 2

Tast (1, 3) and DP (2, 4) polarograms of BDTSDA ( $c = 0.3 \text{ mmol l}^{-1}$ ) (1, 2) and of the supporting electrolyte alone (3, 4). Medium:  $0.01 \text{ M}$  solution of tetraethylammonium bromide in DMF containing 5% (v/v) water

drop time, was constant within the drop time limits of 1–4 s and the mercury reservoir height limits of 25–64 cm. Hence, it can be inferred that the limiting current is due to a diffusion-controlled phenomenon. The shape of the second wave, as well as its logarithmic analysis, indicates an irreversible nature of the process involved, which is also borne out by the absence of any anodic peak during cyclic voltammetry at the HMDE at polarization rates of 50–500 mV s<sup>-1</sup>. The dependence of the position and height of the second DPP peak on the pulse height and polarization rate also bears out the conclusion that this peak is due to an irreversible, diffusion-controlled process. As with the other 4,4'-diaminostilbenedisulfonic acid derivatives studied previously<sup>4,5</sup>, it is impossible to determine unambiguously how many electrons are exchanged in BDTSDA reduction. However, based on reasoning discussed in refs<sup>4,5</sup>, we consider it likely that the observed wave corresponds to the one-electron reduction of BDTSDA to the radical-anion **2**, which is stabilized immediately by accepting a proton as shown in Scheme 1. The subsequent reduction of the formed radical-anion **3** is presumably obscured by the current due to the decomposition of the supporting electrolyte.



SCHEME 1

Comparison of the half-wave potentials of BDTSDA and of 4,4'-bis[(4-phenylamino-6-methoxy-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid<sup>4</sup> and 4,4'-bis[(4-phenylamino-6-morpholino-1,3,5-triazin-2-yl)amino]stilbene-2,2'-disulfonic acid<sup>5</sup> shows that the three compounds cannot be discriminated polarographically, the substituents at the triazine system having virtually no effect on the position of the wave corresponding to the reduction of the double bond in the stilbene system.

The dependences of the wave or peak heights on the BDTSDA concentration in the 0.01 M solution of tetraethylammonium bromide in DMF containing 5% (v/v) water are linear over the concentration region of 0.1–0.5 mmol l<sup>-1</sup> for fast polarography and 0.01–0.5 mmol l<sup>-1</sup> for DPP (Table I). The peak heights were measured from a baseline represented by the straight line connecting the two side minima. Lower concentrations could not be quantitated due to the highly negative half-wave or peak potential. The supporting electrolyte line is smoother if the tetraethylammonium bromide concentration is decreased, bringing about a lowering in the limit of determination.

#### *Differential Pulse Voltammetry Using a Hanging Mercury Drop Electrode*

The parameters of the concentration dependences obtained by this technique are given in Table I. The peak height was measured from the straight line connecting the two side

TABLE I  
Parameters of calibration curves for the polarographic and voltammetric determination of BDTSDA in a 0.01 M solution of tetraethylammonium bromide in dimethylformamide containing 5% (v/v) water

Method	c, mmol l <sup>-1</sup>	Slope mA mol <sup>-1</sup> l	Intercept μA	r <sup>a</sup>	L <sub>Q</sub> <sup>b</sup> μmol l <sup>-1</sup>
TAST/DME	0.1–0.5	22.0	-0.11	0.9992	110
DPP/DME	0.1–0.5	23.2	0.09	0.9989	–
DPP/DME	0.01–0.1	21.3	-0.01	0.9991	8
DPP/DME	0.01–0.1 <sup>c</sup>	15.2	-0.02	0.9988	5
DPV/HMDE	0.1–0.5	17.0	0.4	0.9903	–
	0.01–0.1	17.7	-0.10	0.9970	–
	0.01–0.1 <sup>c</sup>	9.8	-0.02	0.9994	–
	0.001–0.01 <sup>c</sup>	8.2	0.002	0.9986	2
LSV/HMDE	0.1–0.5	13.2	0.5	0.9783	–
	0.01–0.1	20.6	-0.05	0.9884	–
	0.01–0.1 <sup>c</sup>	6.1	-0.01	0.9951	13

<sup>a</sup> Correlation coefficient; <sup>b</sup> limit of determination; <sup>c</sup> 0.001 M tetraethylammonium bromide.

minima. The peak due to the reduction of the double bond and the peak to the reduction of the sodium ions overlap partly at concentrations in excess of  $0.3 \text{ mmol l}^{-1}$ . In such case, a different approach to the evaluation of the peak height must be adopted to preserve the linearity of the dependence: measurement of the distance between the horizontal lines passing through the top of the peak and through the more negative minimum appears to suit best.

A tenfold more dilute solution of tetraethylammonium bromide, giving a smoother supporting electrolyte line, is recommended for BDTSDA concentrations lower than  $0.1 \text{ mmol l}^{-1}$ . As a result, the limit of determination is somewhat lower, despite the fact that lowering the concentration of tetraethylammonium bromide brings about a decrease in the slope of the calibration plot.

#### *Adsorptive Stripping Voltammetry Using a Hanging Mercury Drop Electrode*

The BDTSDA peak height in DPV at a HMDE was found to increase with extending time between the drop formation and the DP voltammogram recording. This is presumably caused by adsorptive accumulation of analyte on the surface of the drop electrode. However, due to the highly negative peak potential and poor reproducibility of the peak heights, adsorptive stripping voltammetry is practically unusable as an analytical method for BDTSDA.

#### *Linear Sweep Voltammetry Using a Hanging Mercury Drop Electrode*

The applicability of this technique to BDTSDA was examined with a view to increasing the sensitivity of determination. However, the limit of determination was considerably higher than for differential pulse voltammetry (Table I).

TABLE II  
Results of determination of BDTSDA in technical products by different methods

Sample	Content, %/Relative standard deviation, % <sup>a</sup>			
	KMnO <sub>4</sub> <sup>b</sup>	Septonex <sup>c</sup>	TAST <sup>d</sup>	DPP <sup>e</sup>
Purified substance <sup>f</sup>	98.9/0.3	98.1/0.3	—	—
Blankophor BSU <sup>g</sup>	47.4/0.5	53.9/0.6	47.9/1.7	47.3/1.3
Rylux BSU <sup>g</sup>	54.6/0.3	56.0/0.4	55.5/1.4	54.1/1.6

<sup>a</sup> The contents are averages of three determinations, from which the relative standard deviation was also calculated; <sup>b</sup> oxidimetric titration with potassium permanganate; <sup>c</sup> precipitation titration with Septonex; <sup>d</sup> tast polarography; <sup>e</sup> differential pulse polarography; <sup>f</sup> sample employed to obtain the calibration plots for tast and DPP analysis; <sup>g</sup> commercial product.



*Practical Application of the Methods Developed*

Practical applicability of the methods was tested by determining BDTSDA in the technical products Blankophor BSU and Rylux BSU as described in the Experimental. The results (Table II) agree very well with those obtained by oxidimetric titration. Moore's u-test gave evidence that the results of the polarographic and oxidimetric determinations did not differ at the 95% confidence level. The slightly higher values obtained by titration with Septonex were apparently due to the presence of other anion-active substances in the commercial products; this presence did not bring about distortion of the polarographic curves. Nevertheless, if complex practical samples were to be analyzed, it would be better to use the standard additions method or to separate BDTSDA from the sample by TLC as described in ref.<sup>5</sup>. The methanol-ethyl acetate 2 : 1 mobile phase proved to suit well to the treatment of Blankophor BSU and Rylux BSU. The choice of the mobile phase for the analysis of environmental samples such as wastewaters would be dependent on the nature of interferences present.

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