POLAROGRAPHIC AND VOLTAMMETRIC DETERMINATION OF 7-[4-METHYL-5-PHENYL-2-(1,2,3-TRIAZOLYL)]-3-PHENYLCOUMARIN

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Received January 18, 1993
Accepted March 27, 1993

The polarographic behaviour of the optical whitening agent 7-[4-methyl-5-phenyl-2-(1,2,3-triazolyl)]-3-phenylcoumarin was studied in mixed aqueous-methanolic solutions. Conditions were found for quantitating the substance by tast polarography, differential pulse polarography, differential pulse voltammetry at a hanging mercury drop electrode, and adsorption stripping voltammetry over the concentration regions of 2 – 10, 0.1 – 10, 0.02 – 1 and 0.004 – 1 μmol l^{-1}, respectively. The methods developed were applied to a direct determination of the substance in a technological product.

7-[4-Methyl-5-phenyl-2-(1,2,3-triazolyl)]-3-phenylcoumarin (see formula *I* in Eq. (*A*); CAS name 7-(4-methyl-5-phenyl-2*H*-1,2,3-triazolyl)-3-phenyl-2*H*-1-benzopyran-2-one, CAS Registry No. 19683-09-1) is an optical whitening agent which is produced on an industrial scale. This substance (henceforth referred to as MPTPC) is added to washing powders and is used for whitening polyacrylates and polyesters[1]. Although modern whitening agents are not supposed to pose health or environmental hazards, some derivatives of coumarin are known to cause photosensitization and exhibit mutagenic activity[2,3]. Availability of sensitive methods for the determination of trace amounts of such substances, which come into the environment in wastewaters from households, laundries and the textile and paper industries, is therefore desirable.

MPTPC can be determined, for instance, spectrophotometrically in the UV region after separation by thin layer chromatography, spectrofluorimetrically, or by high performance liquid chromatography with UV photometric or spectrofluorimetric detection[2].

The polarographic behaviour of coumarin-based optical whitening agents has not received due attention till now. According to Harle and Lyons[4], coumarin in various aqueous buffers gives a single irreversible wave with $E_{1/2}$ = –1.57 V vs SCE, independent of pH. This wave is overlapped by the hydrogen reduction wave at pH < 4, and decreases due to hydrolysis of the substance at pH > 9.3. The authors suggest a one-electron reduction mechanism followed by formation of the dimer. Capka and

Opavsky[5], however, report that the $E_{1/2}$ value of coumarin shifts by 25 mV per pH unit to more negative values within the region of pH 4.8 – 7.5 and remains constant at pH > 10 only. The wave is of diffuse nature, and based on a comparison with the wave of acetophenone the authors suggest that the wave height corresponds to the two-electron reduction of the C=C double bond in the α-position of the lactone ring. The first reduction step gives rise to a free radical which is subsequently reduced as far as the saturated carbonyl compound, the rate of this reduction being higher than that of the dimerization if feasible. However, based on potentiostatic coulometry measurements and identification of the product[4], Perrin[6] considers the one-electron mechanism more probable. This mechanism is also favoured by Griffiths and Westmore[7] and by Knobloch[8], who, however, differentiates between the one-electron reduction of coumarin and the two-electron reduction of methoxycoumarin. The effect of UV radiation on the opening of the coumarin lactone ring has also been investigated polarographically[9]. Great attention has been paid to the effect of the kind and position of substituents on the polarographic behaviour of coumarin derivatives[10 – 15]. Hydroxy and alkyloxy derivatives give a wave whose position is pH-dependent, whereas for alkyl derivatives the pH-dependence is small if any[12]. The methyl group stabilizes the conjugated system appreciably[12], substitution in position 3 of the coumarin ring being most important for the electron delocalization[13,14]. Some substituents can affect the electron delocalization to the extent that the otherwise inactive carbonyl rather than the C=C bond is reduced[13]. At pH > 9, the situation is complicated by the hydrolysis of coumarin and formation of the *cis*-coumarate ion which can give a wave at more negative potentials, as found during the study of some 3-phenylcoumarins in unbuffered solutions[15]. Other papers deal with the polarographic behaviour of coumarin[7,16], 4-hydroxycoumarins[8,11,17] and the insecticide *O,O*-diethyl-*O*-(4-methyl-coumarinyl)-7-thiophosphate[18]. The coumarin derivative novobiocin does not reduce, within the region examined, at a potential more positive than –2.0 V (ref.[19]). No mention, however, has been found in the literature of the application the modern polarographic methods, viz. differential pulse polarography (DPP), differential pulse voltammetry (DPV) at a hanging mercury drop electrode (HMDE), and adsorption stripping voltammetry (AdSV), to the determination of low concentrations of coumarin derivatives. This topic is therefore the subject of the present work.

EXPERIMENTAL

Reagents

7-[4-Methyl-5-phenyl-2-(1,2,3-triazolyl)]-3-phenylcoumarin (Bayer, Leverkusen, Germany) was obtained from the technical product Blankophor EBL by triple recrystallization from hot methanol (the substance is suspended in the commercial product in a triethanolamine solution in a concentration of approximately 10 wt.%). Stock solution in methanol (c = 400 μmol l^{-1}) was prepared by dissolving 0.1398 g of the substance in the solvent and diluting to 1 000 ml. More dilute solutions were ob-

tained by diluting the stock solution with methanol. The purity of the substance was checked by measuring the melting temperature (161 °C, consistent with the published value[2]), by UV spectral measurements of dimethylformamide solutions (the band positions are consistent with published data[2]) and by thin layer chromatographic measurements, which gave a single spot using toluene–chloroform 2 : 3, toluene–chloroform–ethyl acetate 2 : 3 : 1 and 4 : 12 : 1, and benzene–chloroform 2 : 3 mobile phases (R_F = 0.53, 0.92, 0.71 and 0.63, respectively).

Britton–Robinson buffers[20] and ammoniacal buffer[21] were prepared conventionally. The chemicals were of reagent grade purity (Lachema, Brno, The Czech Republic), water was redistilled from a quartz still.

A commercial thin-layer chromatography kit equipped with Silufol UV 254 plates (Kavalier, Votice, The Czech Republic) was employed.

Apparatus

A PA 4 polarographic analyzer equipped with an SMDE 1 mercury drop electrode and interfaced to an XY-4105 recorder (all Laboratorni Pristroje, Prague, The Czech Republic) was used. The SMDE 1 was employed as the working electrode in the static mercury drop electrode mode (SMDE) or in the hanging mercury drop electrode mode (HMDE) with a capillary 0.138 mm in diameter; the maximum drop size was determined by the time of valve opening, which was 160 ms. Alternatively, a conventional mercury drop electrode was used, with the following parameters: mercury reservoir height h = 36 cm, drop time τ = 7.04 s (in 0.1 M NaCl at 0 V vs SCE), mass flow rate m = 0.61 mg s^{-1}. A saturated calomel electrode (relative to which all the voltage data are given) and an auxiliary platinum sheet electrode were used. Oxygen was removed by nitrogen purging from the solutions to be polarographed. Nitrogen was purified for this by passing it through a solution of chromium(II) ions in dilute hydrochloric acid (1 : 1) over zinc amalgam. Before entering the measuring cell, the nitrogen was passed through a bubbler containing the same supporting electrolyte as the cell. All measurements were accomplished at room temperature.

Acidity was measured with an OP-208/1 Precision Digital pH-meter (Radelkis, Hungary) using a combined glass–saturated calomel electrode. The true pH of the buffer–methanol 1 : 1 mixture was determined with this electrode, calibrated by means of buffer solutions in 50 vol.% methanol[22,23].

Spectrophotometric measurements were accomplished on a Pye–Unicam PU 8800 UV-VIS instrument (Philips) using quartz cells 1 or 2 cm optical pathlength.

Small volumes of solutions were added by means of Varipipette 3000 and micropipettes types A-20, A-200 and A-1000 (Plastomed, Poland).

An M 415 centrifuge (Chirana, The Czech Republic) and a rotary vacuum evaporator type 350 (Unipan, Poland) were used during the purification and separation procedures.

Unless stated otherwise, the following conditions were adjusted for the polarographic and voltammetric measurements: potential sweep rate 5 mV s^{-1} in tast polarography and DPP and 20 mV s^{-1} in DPV at HMDE, electronically controlled drop time 1 s, and DME reservoir height 36 cm. The DPP and DPV pulse height was –50 mV.

Procedures

For the polarographic and voltammetric measurements, a preselected volume of MPTPC solution in methanol at the required concentration was pipetted into a 10 ml volumetric flask, methanol was added, and the solution was diluted to volume with the appropriate Britton–Robinson buffer. This order of addition had to be adhered to because if the methanolic solution of MPTPC is added to the aqueous buffer, the analyte may separate from the solution. The buffer solutions and methanol must

be kept in glass vessels rather than in polyethylene, from which substances affecting adversely the determination of low concentrations of MPTPC are extracted.

The polarographic/voltammetric curves were recorded following a 10 min nitrogen purging of the solution. The calibration curves were measured in triplicate and processed statistically.

The limit of determination L_Q was determined as the tenfold standard deviation from seven determinations of the analyte at the concentration corresponding to the lowest point of the calibration curve[24].

The following procedure was applied to quantitate MPTPC in Blankophor EBL by DPP at the DME: 35.0 mg of Blankophor EBL were dissolved in a small volume of methanol and diluted to 100 ml in a volumetric flask. A 0.1 ml aliquot was transferred into a 10 ml volumetric flask, 4.90 ml of methanol were added, the whole was diluted to the mark with the Britton–Robinson buffer pH 4.3, and the differential pulse polarogram was recorded. The MPTPC content was read from a calibration straight line plot obtained by using the pure substance.

The procedure for quantitating MPTPC in Blankophor EBL by UV spectrophotometry was as follows: 35.0 mg of Blankophor EBL were dissolved in a small volume of methanol, the solution was diluted to 100 ml in a volumetric flask, and the absorption spectrum in the UV region was run. The MPTPC content was again read from a calibration straight line plot obtained by measuring solutions of the pure substance.

RESULTS AND DISCUSSION

Stability of MPTPC Stock Solutions

The absorption spectrum of MPTPC in methanol exhibits maxima at 231 and 356 nm (Fig. 1). The validity of Beer's law was verified over the region of 2 – 400 μmol l^{-1}; the molar absorptivity calculated from the absorbance vs concentration plot was $\varepsilon_{356} = 6.29 \cdot 10^4$ l mol^{-1} cm^{-1}. The absorbance of MPTPC stock solutions in methanol at c = 5, 50 and 400 μmol l^{-1}, kept in dark, was constant within the limits of experimental

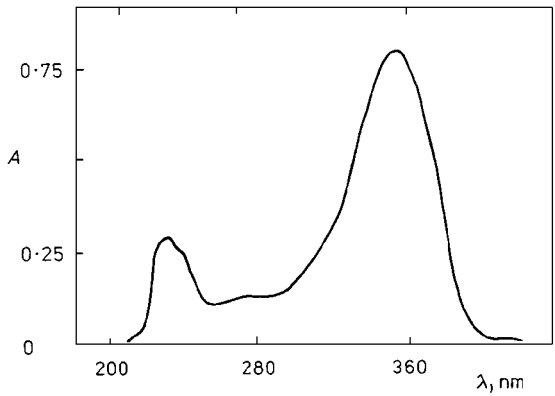


FIG. 1
Absorption spectrum of MPTPC (c = 12 μmol l^{-1}) in methanol. Optical pathlength 1 cm

error for a fortnight and did not decrease more than 1% in a month. Fresh solutions at lower concentrations were prepared daily.

Tast Polarography and Differential Pulse Polarography of MPTPC

With regard to the low solubility of MPTPC in water, the effect of the methanol content on the polarographic behaviour was investigated at various pH values (Table I). The tast polarography wave height was measured on a line parallel to the electric current axis and passing through the half wave potential; the value was determined as the distance of two non-parallel straight lines obtained by construction in the region before the wave and in the limiting current region. The DPP peak height was measured from the straight line connecting the minima on the two sides of the peak. Selected DP polarograms are shown in Fig. 2. The wave or peak height decreases markedly with decreas-

TABLE I
Effect of methanol content φ_{MeOH} (vol.%) in Britton–Robinson buffer–methanol mixtures on the limiting current I_{lim} (μA) in tast polarography and on the peak height I_p (μA) in differential pulse polarography of MPTPC (c = 10 μmol l^{-1})

φ_{MeOH}	pH[a]	I_{lim}	I_p	pH[b]	I_{lim}	I_p	pH[c]	I_{lim}	I_p
2.5	3.5	0.19	0.30	4.3	0.19	0.32	7.9	0.11	0.18
5.0	3.5	0.11	0.15	4.4	0.07	0.12	7.9	0.05	0.11
10.0	3.5	0.03	0.04	4.4	0.04	0.08	8.0	0.05	0.10
20.0	3.8	0.04	0.05	4.7	0.06	0.10	8.2	0.08	0.12
50.0	4.2	0.90	1.89	5.0	0.84	1.90	8.5	0.19	0.25
75.0	4.7	2.41	2.21	5.6	1.63	2.20	8.9	0.23	0.45

Buffer pH: [a] 3.45, [b] 4.30, [c] 7.81.

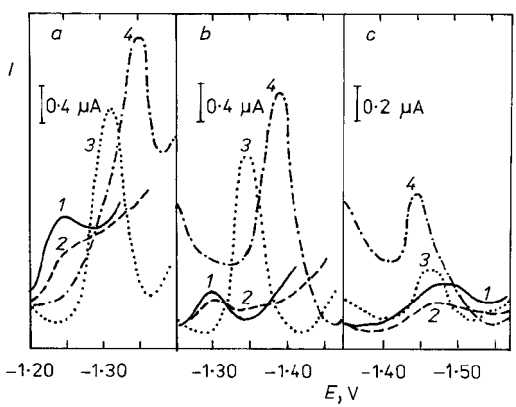


FIG. 2
Effect of the methanol content on DP polarograms of MPTPC (c = 10 μmol l^{-1}) in Britton–Robinson buffer–methanol mixtures. Buffer pH: *a* 3.45, *b* 4.30, *c* 7.81. Methanol content (vol.%): *1* 2.5, *2* 10, *3* 50, *4* 75

ing methanol content, which is presumably due to the low analyte solubility in aqueous medium. With regard to the wave or peak shape, 50 vol.% methanolic solutions were used in the subsequent measurements.

The effect of pH on the polarographic behaviour of MPTPC at c = 10 μmol l^{-1} was studied in a solution containing 50 vol.% Britton–Robinson buffer (pH 2 – 12) and 50 vol.% methanol (Table II). Selected DP polarograms are shown in Fig. 3.

TABLE II
Effect of pH on tast and DP polarograms of MPTPC (c = 10 μmol l^{-1}) in Britton–Robinson buffer–methanol 1 : 1 mixtures

pH[a]	pH[b]	$E_{1/2}$[c] V	I_{lim}[d] μA	E_p[e] V	I_p[f] μA
2.18	2.4	–1.22[g]	0.7[g]	–1.152	2.0
2.70	3.4	–1.26[g]	0.9[g]	–1.220	1.8
3.45	4.2	–1.316	0.9	–1.304	1.9
4.30	5.0	–1.362	0.8	–1.341	1.8
4.99	5.7	–1.423	0.5	–1.402	0.5
6.01	6.9	–1.488	0.3	–1.450	0.3
6.48	7.3	–1.484	0.2	–1.462	0.2
7.81	8.5	–1.497	0.2	–1.467	0.2
9.07	9.5	–1.512	0.2	–1.463	0.2
11.43	11.8	–1.520	0.2	–1.469	0.2

[a] Buffer; [b] aqueous-methanolic medium; [c] half-wave potential in tast polarography; [d] limiting current in tast polarography; [e] peak potential in DPP; [f] peak height in DPP; [g] crude value, polarogram was difficult to evaluate.

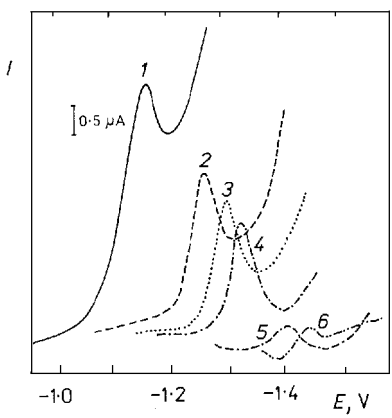
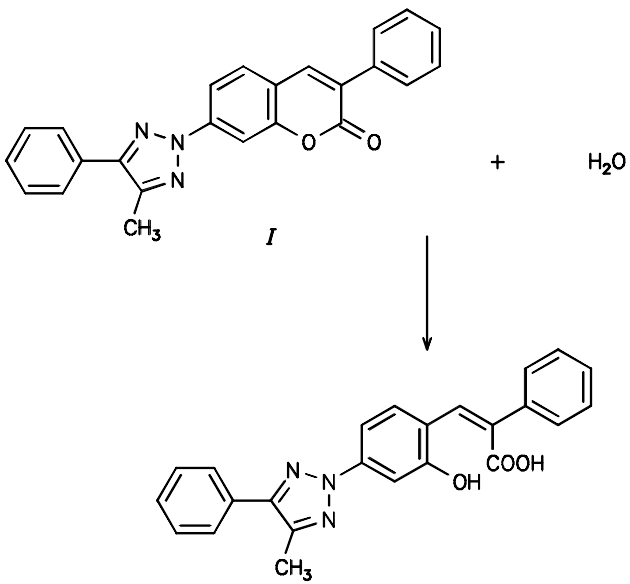


FIG. 3
Effect of pH on DP polarograms of MPTPC (c = 10 μmol l^{-1}) in Britton–Robinson buffer–methanol 1 : 1 mixtures at pH: *1* 2.4, *2* 3.4, *3* 4.2, *4* 5.0, *5* 5.7, *6* 9.5

Over the region of pH 2 – 6, the $E_{1/2}$ as well as the E_p values shift to more negative potentials with increasing pH, the slope of this linear dependence being 66 mV per pH unit in tast polarography and 70 mV per pH unit in DPP. The $E_{1/2}$ and E_p values remain constant at pH > 7.

The wave or peak height is virtually constant within the pH 2 – 5 range. The waves are difficult to evaluate at pH < 3 because they are superimposed by the hydrogen ion reduction wave. At pH > 5, the MPTPC wave or peak decreases, presumably due to alkaline hydrolysis of the substance according to Eq. (*A*).



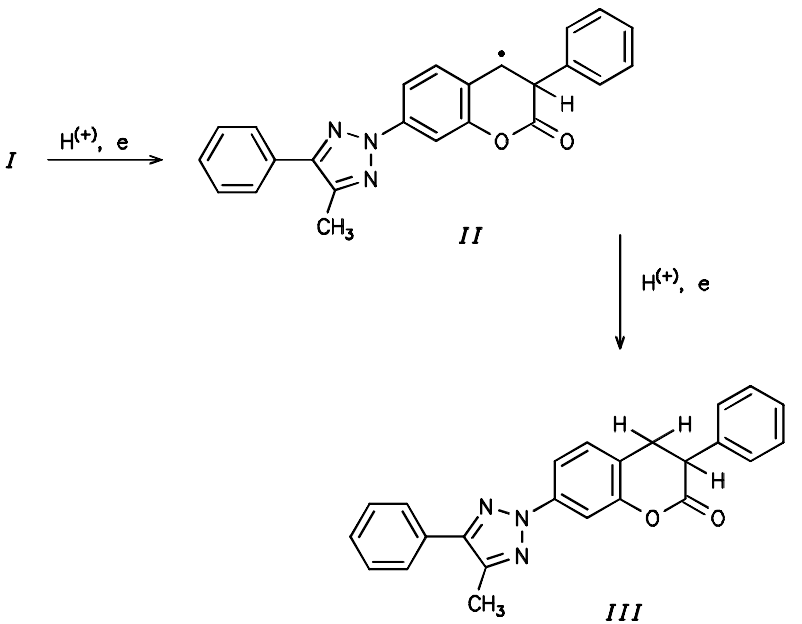
I (*A*)

This assumption is borne out by the fact that the height of the DPP peak of the compound (c = 10 μmol l^{-1}) in a Britton–Robinson buffer–methanol 1 : 1 mixture at pH 9.5 decreases from the 0.45 μA observed 2 min after adding the substance to the solution, to 0.14, 0.10 and 0.06 μA in 15, 30 and 60 min, respectively (a similar effect has been described for other coumarin derivatives as well[4,9]). Logarithmic analysis of the tast polarographic curves and cyclic voltammetry measurements at a hanging mercury drop electrode give evidence that an irreversible phenomenon is involved, and the observed linear dependence of the DC polarographic wave height on the mercury reservoir height square root in Britton–Robinson buffer–methanol 1 : 1 solution at pH 5.0 indicates the diffusion nature of the limiting current.

However, comparison with the polarographic behaviour of unsubstituted coumarin, which in the Britton–Robinson buffer–methanol 1 : 1 medium at pH 5 – 9 reduces at

$E_{1/2}$ = −1.55 V, hence, a value which is more negative than that for the reduction of MPTPC, indicates that the mechanisms of reduction of the two compounds are different. This is also borne out by the fact that the observed limiting current of MPTPC within the pH 2 – 5 range is nearly double as compared to that of coumarin.

In view of the +M effect of the aromatic ring in position 3 of the coumarin ring, the half-wave potential of MPTPC should shift to more negative values as compared to unsubstituted coumarin. The actual shift is opposite, which may be due to the fact[11] that the phenyl ring in position 3 is not coplanar with the coumarin ring so that conjugation cannot occur. An alternative cause consists in the appreciable electron delocalization, which – as in some other coumarin derivatives[13] – brings about reduction of the otherwise inactive carbonyl group at potentials more positive than as would correspond to the reduction of the C=C bond in a substance analogous to MPTPC but having no aromatic ring in position 3. The former alternative seems more probable: this includes two-electron reduction of MPTPC according to scheme (*B*), analogous to the reduction of esters of α,β-unsaturated carboxylic acids[25] and other α,β-unsaturated carbonyl compounds[26]. In view of the observed height of the MPTPC wave, the rate of dimerization of the transient radical *II*, if occurring, is lower than the rate of the consecutive reduction to the saturated carbonyl compound *III*.



(*B*)

The Britton–Robinson buffer–methanol 1 : 1 mixture at pH 5.0 appears optimal from the analytical point of view, the waves and peaks obtained in it being best developed and best suited to evaluation (Fig. 3). The dependence of the wave or peak height on the analyte concentration is linear over the region of 2 – 10 μmol l^{-1} for tast polarography and 0.02 – 10 μmol l^{-1} for DPP. The parameters of the dependences are given in Table III. Higher concentrations of MPTPC cannot be quantitated with regard to the low analyte solubility in the supporting electrolyte. Dilution of the buffer or lowering of the methanol content of the supporting electrolyte did not bring about decrease in the limit of determination. Tast and DP polarograms corresponding to the lowest attainable concentration range are shown in Fig. 4.

TABLE III

Parameters of the dependence of limiting current I_{lim} in tast polarography and peak height I_p in DPP at a DME on the concentration of MPTPC in Britton–Robinson buffer–methanol 1 : 1 mixture at pH 5.0

Method	c mol l^{-1}	Slope mA mol^{-1} l	Intercept μA	r^a	$L_Q{}^b$ μmol l^{-1}
Tast	$(1 - 10) . 10^{-6}$	75	0.02	0.9980	1.8
DPP	$(1 - 10) . 10^{-6}$	195	–0.05	0.9993	–
	$(1 - 10) . 10^{-7}$	168	–0.008	0.9986	–
	$(1 - 10) . 10^{-8}$	148	–0.002	0.9964	0.05

[a] Correlation coefficient; [b] limit of determination.

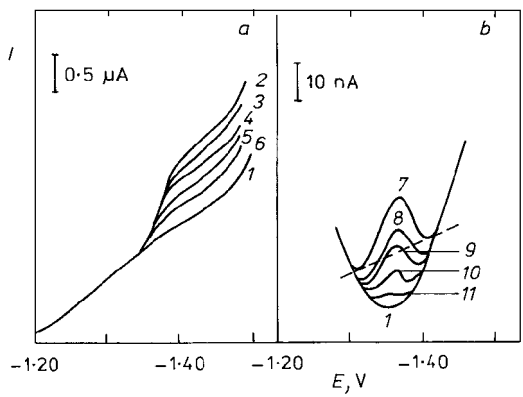


FIG. 4

Tast (*a*) and DP (*b*) polarograms of MPTPC in Britton–Robinson buffer–methanol 1 : 1 mixtures, pH 5.0. Analyte concentration (μmol l^{-1}): *1* 0, *2* 10, *3* 8, *4* 6, *5* 4, *6* 2, *7* 0.1, *8* 0.08, *9* 0.06, *10* 0.04, *11* 0.02. Broken line is the baseline from which the peak height was read

The effect of pH on the DPV behaviour of MPTPC using an HMDE is documented in Table IV. Tenfold diluted Britton–Robinson buffer, which gives a smoother supporting electrolyte baseline, was employed. The character of the dependences is similar to that of the tast and DPP dependences. The slope of the E_p vs pH dependence over the pH 3 – 7 range is 48 mV per pH unit. The Britton–Robinson buffer–methanol 1 : 1 mixture at pH 5.0 emerged as optimum with respect to the peak shape and height at low concentrations.

In agreement with the theory, the peak height increases both with the drop size and with the modulation amplitude. In the latter case, however, the peak width increases with the amplitude as well, and therefore the maximum drop size determined by the valve opening period of 160 ms and a modulation amplitude of –50 mV were chosen as the optimum.

In such conditions the dependence of the peak height on the concentration of MPTPC is linear across the region of 0.01 – 1 μmol l^{-1}. The parameters of this dependence, along with the calculated values of the limit of determination, are given in Table V.

In order to make the method more sensitive, the possibility was examined of applying preliminary adsorptive accumulation of the analyte from the unstirred solution on the hanging mercury drop electrode, followed by DPV measurement. In fact, the electrocapillary curves of coumarin[7] give evidence of a strong adsorption of this sub-

TABLE IV
Effect of pH on DP voltammograms of MPTPC (c = 1 and 0.2 μmol l^{-1}) at a HMDE. Medium of tenfold diluted Britton–Robinson buffer–methanol 1 : 1

pH[a]	E_p[b,c] V	I_p[d,e] μA	I_p[d,f] μA
3.4	–1.26	0.983	0.200
4.3	–1.29	0.801	0.160
5.0	–1.32	0.780	0.156
5.7	–1.37	0.557	0.110
6.9	–1.43	0.358	0.071
7.9	–1.43	0.194	0.042
8.8	–1.43	0.206	0.040
9.5	–1.44	0.217	0.041
11.2	–1.44	0.201	0.038
12.4	–1.43	0.203	0.039

[a] Of the aqueous-methanolic solution; [b] peak potential; [c] values corresponding to the higher concentration, values corresponding to the lower concentration differ in the third decimal place; [d] peak height; [e] c = 1 μmol l^{-1}; [f] c = 0.2 μmol l^{-1}.

stance to the mercury drop electrode surface. Really, the height of the peak of MPTPC was found to increase considerably on applying such procedure (Fig. 5). The I_p value was virtually independent of the accumulation potential (–0.4, –0.8 and –1.15 V). An accumulation period of 60 s was chosen.

TABLE V
Parameters of the dependence of the DPV peak height (HMDE) on the concentration of MPTPC in a 1 : 1 mixture of tenfold diluted Britton–Robinson buffer with methanol at pH 5.0

c mol l^{-1}	t_{acc} [a] s	Slope mA mol^{-1} l	Intercept nA	r [b]	L_Q [c] μmol l^{-1}
$(1 - 10) . 10^{-7}$	0	750	14	0.9997	–
	60	2 245	–21	0.9993	–
$(1 - 10) . 10^{-8}$	0	600	–4.8	0.9970	0.018
	60	1 900	1.0	0.9997	–
$(1 - 10) . 10^{-9}$	60	2 800	0.2	0.9976	0.0038

[a] Time of accumulation; [b] correlation coefficient; [c] limit of determination.

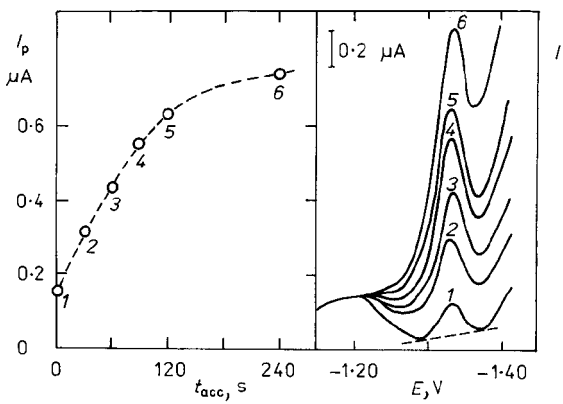


FIG. 5
Effect of time of accumulation on the DP voltammograms of MPTPC (c = 0.2 μmol l^{-1}) at a HMDE. Medium of tenfold diluted Britton–Robinson buffer–methanol (1 : 1) at pH 5.0. Time of accumulation t_{acc} (s): *1* 0, *2* 30, *3* 60, *4* 90, *5* 120, *6* 240. Broken line is the baseline from which the peak height was read

In such conditions, linear concentration dependences were obtained across the region of 0.002 – 1 μmol l^{-1}, hence, the limit of determination is one order of magnitude lower if adsorptive accumulation is applied. This value could not be decreases further by using a hundredfold more dilute buffer or by reducing the methanol content.

Practical Application

The DPP method using a DME was used to determine the MPTPC content in the technical product Blankophor EBL, as described in the Experimental. The MPTPC content found was 10.5%, with a standard deviation estimate of 0.53% calculated from the range of three analyses. The spectrophotometric method gave a content of 9.6% MPTPC, the standard deviation estimate, calculated likewise, was 0.35%. Moore's u-test showed that the results of the polarographic and spectrophotometric analysis do not differ at the 95% confidence level. If MPTPC were to be determined polarographically in waste waters, a suitable preliminary separation method would have to be used, in dependence on the composition of the matrix, e.g. extraction combined with thin layer chromatography[2].

REFERENCES

1. Sarkar A. K.: *Fluorescent Whitening Agents*. Merrow Publ., Watford 1971.
2. Anliker R., Muller G. in: *Environmental Quality and Safety* (F. Coulston and F. Korte, Eds), Vol. IV. Thieme, Stuttgart 1975.
3. Marhold J.: *Prehled prumyslove toxikologie*, Vol. 2. Avicenum, Praha 1986.
4. Harle A. J., Lyons L. E.: J. Chem. Soc. *1950*, 1575.
5. Capka O., Opavsky J.: Collect. Czech. Chem. Commun. *15*, 965 (1950).
6. Perrin Ch. in: *Progress in Physical Organic Chemistry* (S. G. Cohen, A. J. Streitwieser and R. W. Taft, Eds), Vol. III, p. 229. Wiley, New York 1965.
7. Griffiths V. S., Westmore J. B.: J. Chem. Soc. *1962*, 1704.
8. Knobloch E.: *Proceedings of 2nd International Congress on Advances in Polarography, Cambridge 1959*. Vol. 3, p. 875.
9. Patzak R., Neugebauer L.: Monatsh. Chem. *82*, 662 (1951).
10. Orlov M. E., Prokopenko A. P.: Zh. Obshch. Khim. *40*, 1159 (1970).
11. Van Zanten B., Nanta W. Th.: Arzneim.-Forsch. *14*, 29 (1964).
12. Patzak R., Neugebauer L.: Monatsh. Chem. *83*, 776 (1952).
13. Dezelic R., Trkovnik L.: Croat. Chem. Acta *33*, 209 (1961).
14. Dezelic R., Trkovnik L.: Croat. Chem. Acta *35*, 43 (1963).
15. Archer J. F., Grimshaw J.: J. Chem. Soc., B *1969*, 266.
16. Brook P. A., Crossley J. A.: Electrochim. Acta *1966*, 1189.
17. Wawzonek S., McIntyre T. W.: J. Electroanal. Chem. *12*, 544 (1966).
18. Kovac J.: Chem. Zvesti *8*, 272 (1954).
19. Hruman J. W., Caron E. L., Hoekseme H.: J. Am. Chem. Soc. *79*, 3789 (1957).
20. Sykora V.: *Chemickoanalyticke tabulky*. SNTL, Praha 1976.
21. Cihalik J., Dvorak J., Suk V.: *Prirucka mereni pH*. SNTL, Praha 1975.

22. Paabo M., Robinson R., Bates R. G.: J. Am. Chem. Soc. *87*, 415 (1965).
23. Kozakova E., Csefelvayova B.: Chem. Zvesti *34*, 610 (1980).
24. Beyermann K.: *Organic Trace Analysis*, p. 42. E. Horwood, Chichester 1984.
25. Elving P. J., Teitelbaum Ch.: J. Am. Chem. Soc. *71*, 3916 (1949).
26. Pasternak R.: Helv. Chem. Acta *31*, 753 (1948).

Translated by P. Adamek.