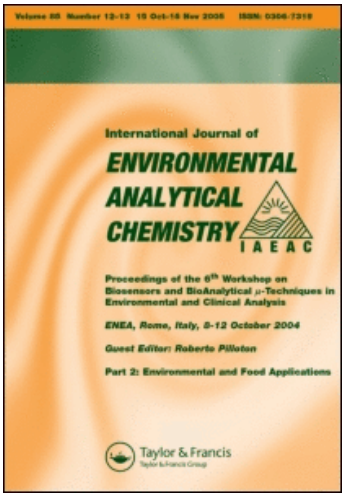

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Electrochemical reduction behaviour of the synthetic pyrethroid insecticide cyfluthrin and its determination in formulations and environmental samples

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The polarographic behaviour of cyfluthrin (CY), an α-cynoester pyrethroid, was studied using a dropping mercury electrode and hanging mercury drop electrode in methanolic Britton–Robinson (B–R) buffer of pH 2.0–12.0 with different ionic media. The nature of the electrode process was examined, the number of electrons was evaluated, and the reduction mechanism was proposed. Quantitative determination was achieved in the concentration range of 6.0×10^{-8} to 1.15×10^{-5} mol dm^{-3} using a differential pulse polarographic method with a lower detection limit of 2.4×10^{-8} mol dm^{-3}. The proposed method was successfully applied in the determination of CY in formulations, grains, soils, and spiked water samples.

Keywords: Cyfluthrin; Electrochemical reduction; Formulations; Environmental samples

1. Introduction

Pyrethroids are an interesting class of compounds and are widely used worldwide [1, 2]. Cyfluthrin (figure 1) [cyano-(4-fluoro-3-phenoxybenzyl)-methyl-(2,2-dichlorovinyl)-2,2-methyl cyclopropane carboxylate] is a synthetic type II pyrethroid and acaricide, is effective against many types of pests of plants and vegetables, and is also used for domestic applications. It is present in the market in a variety of formulations as a wettable powder, emulsifiable concentrations, oil-in-water emulsions, and dusts. Large dosages of cyfluthrin cause excess salivation, irritability, and a fall in blood pressure. It has been demonstrated to be toxic to mammals, with an acute oral LD_{50} value of 16 mg kg^{-1}. Therefore, its content needs to be controlled. A number of analytical techniques, mostly chromatographic methods, are reported in the literature for the determination of synthetic pyrethroids.

Electrochemical studies of the same group pyrethroid insecticides are performed using mercury and glassy carbon electrodes [3–7]. The electrochemical behaviour of

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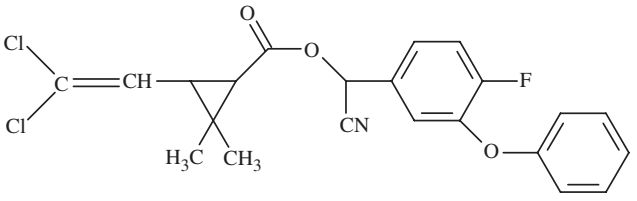


Figure 1. Structure of cyfluthrin.

cyfluthrin at the glassy carbon electrode in non-aqueous solutions has been reported [6]. The present communication reports the electroanalytical determination of cyfluthrin using DME and HMDE in aqueous solutions, formulations, grains, soils, and spiked water samples.

2. Experimental

2.1 *Apparatus*

A Metrohm-E-506 (Herisau, Switzerland) Polarecord equipped with a Metrohm 663 VA stand was used for direct current polarography (DCP) and differential pulse polarography (DPP) measurements. Cyclic voltammetric (CV) measurements were performed with a Metrohm-757-VA computrace. The electrode assembly consisted of DME, HMDE as working electrodes, a saturated Ag/AgCl(s), Cl^- reference electrode, and glassy carbon as auxiliary electrode. pH measurements were carried out with a Metrohm (Herisau, Switzerland)-632 pH meter. All measurements were carried out at room temperature ($21 \pm 3^\circ C$). By using solvent extraction, soil samples were extracted, and preconcentration of water samples was performed with Sep-Pack plus C_{18} cartridge. An ordinary rotatory vacuum evaporator was used for evaporation of the solvents. ^1H NMR spectra were recorded on a Varian EM-360 spectrometer in $CDCl_3$ in the presence of $SiMe_4$ as an internal standard. Controlled potential electrolysis was performed with a Techno Potentiostat (Model PS-603). HPLC analyses were carried out with a Waters 510 (Milford, MA) pump and a Rheodyne (Cotati, CA) Model 7125 injector fitted with a 20 µL loop. The photodiode array detector employed was a Waters 996 model. A μ-Bondapack C18 300×3.9 mm i.d. (10 µm) HPLC column with a μ-Bondapack C18 Guard-pack precolumn insert (waters) was used.

2.2 *Reagents and solutions*

Cyfluthrin (95%) [Bayer (I) Ltd], Mumbai was used without any further purification. Stock standard solution of CY (1×10^{-3} mol dm^{-3}) was prepared in methanol. All solvents used were of HPLC grade, and salts used for ionic media were of analytical reagent grade. Cyfluthrin formulations were obtained from local dealers of agrochemicals. Triple-distilled water was used for polarographic measurements. Britton–Robinson (BR) buffer solution was prepared with 0.04 mol dm^{-3} ortho-phosphoric acid (85%), 0.04 mol dm^{-3} acetic acid (99%), and 0.04 mol dm^{-3} boric acid, and used as a supporting electrolyte. The pH, ranging from 2.0 to 12.0, was adjusted by adding 0.2 mol dm^{-3} sodium hydroxide solution.

2.3 *Procedure*

A standard stock solution (1×10^{-3} mol dm^{-3}) of CY was prepared by the dissolution of a suitable amount of electroactive species in methanol. In a 10 mL volumetric flask, an aliquot of standard solution, 4 mL of (0.04 mol dm^{-3}) BR buffer, 4 mL of methanol and 2 mL of KCl were taken. The solution was made up to 10 mL with deionized water and placed into a polarographic cell. The solution was deoxygenated with oxygen-free nitrogen gas (99%) for 5 min. After the polarograms were recorded, small aliquots of the standard solution were added, and polarograms were recorded after each addition under similar conditions. In the present study, the best precision was obtained at pH 3.0 at a drop time of 1.2 s, pulse amplitude of 30 mV, and applied potential of −0.87 V *versus* Ag/AgCl(s)/Cl$^-$. The relative standard deviation and correlation coefficients were found to be 1.23 and 0.993%, respectively.

2.4 *Analysis*

The polarographic peak attributed to the reduction of unsaturated >C=C< group at pH 3.0 is highly reproducible and was preferred for analysis. Both standard addition and calibration methods were used for the quantitative estimation of the compound. The detection limit was found to be 2.4×10^{-8} mol dm^{-3}. The detection limit (dl) [8] was calculated using the expression dl = 3SD/m, where 'SD' is the standard deviation, and m the slope of the calibration graph.

3. Results and discussion

In order to select a suitable solvent, supporting electrolyte, and ionic media for the electrochemical investigations of CY, the mixtures of acetone, acetonitrile, and methanol with water as solvents were used. Supporting electrolytes employed were perchloric acid, hydrochloric acid, acetate buffer, phosphate buffer, BR buffer, KCl, KNO_3, $NaClO_4$, and NaCl salts for ionic media. BR buffer (0.04 mol dm^{-3}) and KCl (0.05 mol dm^{-3}) gave the most well-defined signal.

The polarographic behaviour of CY was studied in the pH range 2.0–12.0 using DCP, DPP, and CV techniques. The compound gave a single well-defined signal up to pH 9.0. As the pH increased from 9.0, another peak also appeared, and both merged into a single peak from pH 10.0. A shift of E_p values towards more negative potentials with increasing pH is observed, which indicates proton participation in the reduction process. The peaks in acidic and neutral medium were attributed to the reduction of the unsaturated >C=C< group in a two electron process. In alkaline medium, because of hydrolysis of the ester group, cleavage occurs in the molecule and gives the products chloro-chrysanthemum acid, 4-fluoro, 3-phenoxy benzaldehyde, and a cyanide ion, which abstracts proton from the solvent or electrolyte and forms as HCN [9–11]. The peak at −1.3 V was due to the reduction of 4-fluoro-3-phenoxy benzaldehyde to 4-fluro3-phenoxy benzyl alcohol. The reduction mechanism in alkaline medium is in agreement with that previously reported for the synthetic pyrethroids [12]. Typical DCP and DPP are shown in figure 2.

The variation of E_p values (where E_p is the peak potential in DPP) towards more negative potentials upon increasing the concentration of electroactive species in DPP

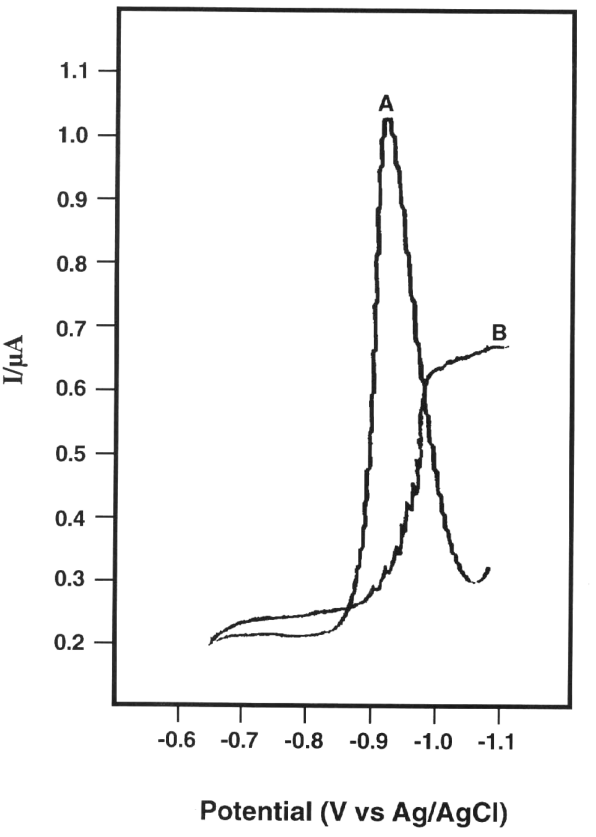


Figure 2. Polarograms of cyfluthrin in pH 3.0. Concentration: 1×10^{-5} mol dm^{-3}; drop time: 1.2 s; pulse amplitude: 30 mV. (a) Differential pulse polarography; (b) direct current polarography.

[13] and the slope value of 28 ± 12 mV for the plot E *versus* $\log(i/i_d - i)$ in DCP indicates that the reduction reaction was irreversible in the pH range studied. The nature of the process was found to be a diffusion-controlled irreversible process in the entire buffer system studied, as evidenced by the linear plots of i_p *versus* $v^{1/2}$ (where i_p is the peak current, and v is the scan rate in CV), the absence of an anodic peak (figure 3), and the relationship of i_p *versus* $\log v$ with slope values of approximately 0.48 ± 0.03 V and 0.055 ± 0.4 between pH 2.0 and 10.0, and between pH 9.0 and 12.0, respectively. The number of protons in the rate-determining step was calculated by using the following equation and was found to be two in the entire pH range.

$$\frac{\Delta E_p}{\Delta pH} = \frac{-0.059}{\alpha n_a},$$

where α is the transfer coefficient.

The value of n_a for the process was calculated from the equation and was found to be 1.6 ± 0.3 ($2.0 \geq pH \leq 10.0$), 2.0 ± 0.2 ($9.0 \geq pH \leq 12.0$)

$$E = E_{1/2} - \left(\frac{0.059}{\alpha n_a}\right) \log\left[\frac{i}{i_d} - i\right].$$

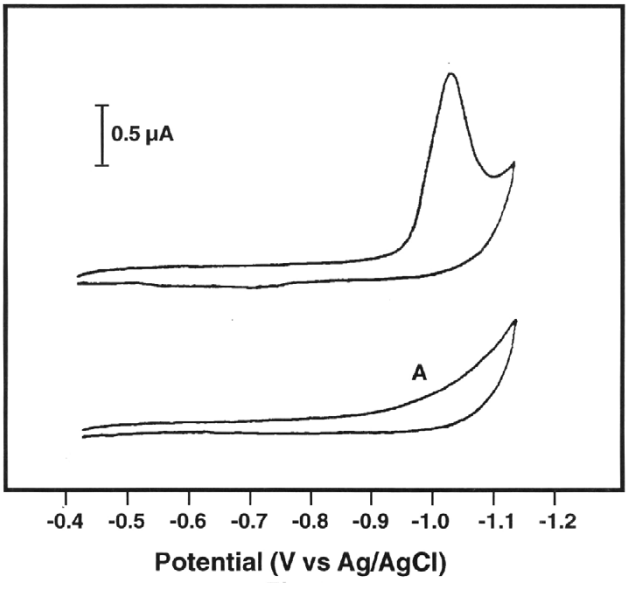


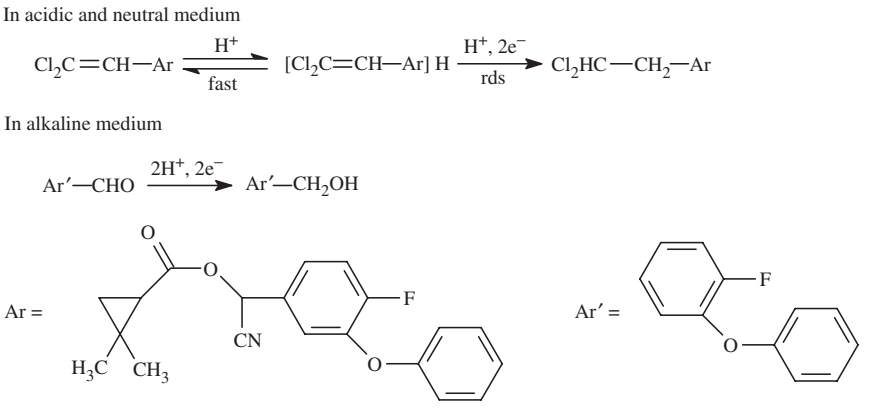
Figure 3. Cyclic voltammogram of cyfluthrin at pH 6.0. Concentration: 1×10^{-5} mol dm^{-3}; sweep rate: 50 mV s^{-1}. (a) Blank.

Controlled potential electrolysis was carried out for the identification of reduction products. Two millilitres of 1×10^{-3} mol dm^{-3} solution of the electroactive species was placed in the cell, and the electrolysis was carried out at a potential of -0.3 V and -1.2 V (*vs.* Ag/AgCl^{-}) up to 8 h by using a mercury pool electrode (area 11 cm^2) at pH 4.0 and 10.0. During the electrolysis, solutions were continuously stirred and purged with nitrogen. After the electrolysis, the solution was extracted three times with 20 mL of cyclohexane. The combined extracts were dried over anhydrous sodium sulphate, and the solvents were removed by evaporation. The reduction products were confirmed by ^{1}H NMR spectra (for the reduction of the >C=C< group: 2.42 (q, 2H, –CH_2–CH–Cl_2), 2.72 (q, 1H, –CO–CH–CH–) 2.78 (s, 6H), 2.80 (q, 2H, –CH_2–$CHCl_2$), 3.12 (d, 1H, –CO–CH–), 6.20 (t, 1H, $CHCl_2$), 7.28–8.18 (m, 9H, 8H_{Arom}, and –CH–CN–)), (for the product 4-fluoro,3-phenoxy benzyl alcohol: 4.54(s, 2H), 5.56 (s, 1H, –OH) 7.32–7.79 (m, 8H, H_{Arom})). The number of electrons transferred in the reduction process was determined using the millicoulometric technique [14] and was found to be two in acidic and basic medium. On the basis of the results of our own investigation as well as data from the literature [15], the following mechanism is proposed in acidic, neutral and basic media (scheme 1).

4. Quantitative study

4.1 *Determination of cyfluthrin in formulations*

A suitable amount of commercial formulation was taken and evaporated to dryness. A stock solution of 1×10^{-3} mol dm^{-3} was prepared by dissolving the formulation



Scheme 1. Electrochemical reduction of cyfluthrin.

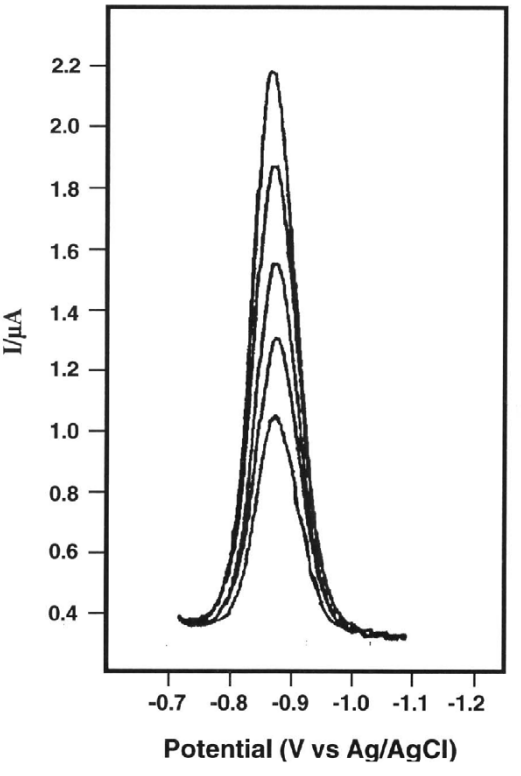


Figure 4. Differential-pulse polargramms obtained from the standard addition determination of cyfluthrin in baygon commerical formulation (20 μL added to 10 mL). Pulse amplitude: 30 mV; peak potential measured at −0.87 V at pH 3.0.

in methanol. An aliquot of stock formulation solution was added to the cell containing buffer. The procedure described above was applied for the determination of CY in formulations using the standard addition method with four additions of stock solution (figure 4). The assay results are given in table 1. These values are compared with values obtained by HPLC.

Table 1. Determination of cyfluthrin in formulations.

Commercial product	Labelled amount (mg)	Average amount found[a] (mg) ± SD		Average recovery (%)	
		By DPP	By HPLC	By DPP	By HPLC
Baygon	5.0	4.93 ± 0.077	4.99 ± 0.012	98.60	99.80
	10.0	10.01 ± 0.089	9.97 ± 0.017	100.10	99.70
	15.0	14.80 ± 0.040	15.00 ± 0.017	98.66	100.00
Baythroid	5.0	4.97 ± 0.016	4.93 ± 0.016	99.40	98.60
	10.0	9.97 ± 0.012	9.94 ± 0.060	99.70	99.40
	15.0	14.95 ± 0.077	15.02 ± 0.042	99.66	100.13
Solfac	5.0	5.01 ± 0.057	4.93 ± 0.014	100.20	98.60
	10.0	9.98 ± 0.080	10.01 ± 0.040	99.80	100.10
	15.0	15.03 ± 0.030	14.95 ± 0.021	100.20	99.66

[a] Each value is an average of three determinations.

Table 2. Recoveries of cyfluthrin added to grains and soils.

Amount added (mg)	Average amount found (mg) ± SD[a]		Average recovery (%)	
	Rice	Soil	Rice	Soil
4.0	3.96 ± 0.099	4.01 ± 0.021	99.0	100.25
8.0	7.95 ± 0.018	7.83 ± 0.038	99.37	97.87
12.0	12.02 ± 0.023	11.99 ± 0.012	100.16	99.91
16.0	15.97 ± 0.017	16.06 ± 0.045	99.81	100.37

[a] Each value is an average of three determinations.

4.2 *Analysis of cyfluthrin in grains*

A grain (rice) sample (50 gm) was ground into a coarse powder, spiked with a known amount of CY, and left for 2–4 h. Then, the sample was extracted with chloroform twice, each time with 100 mL, the mixture transferred into a Buchnner funnel, and then filtered under suction. The extract was transferred into a separating funnel, and then 100 mL of water, 10 mL of saturated sodium chloride, and 50 mL of dichloromethane added. The mixture was shaken for 2 min, and the dichloromethane layer was separated. The extraction was repeated twice with 50 mL portions of dichloromethane. The dichloromethane extracts were combined, 50 g of sodium sulphate was added, and the mixture was then allowed to stand for 30 min. Filtered the dry extract through Buchner funnel under suction, rinsed the contained mixture with three 10 mL portions of dichloromethane and evaporated the solvent through rotatory evaporator. The residue of CY was dissolved in methanol and transferred into 50 mL standard flask. The results obtained for the determination of CY in grains are presented in table 2.

4.3 *Determination of cyfluthrin in soil samples*

Soil samples were air dried, allowed to pass through a 2.8 mm sieve, and subsequently homogenized in a ball mill. An aliquot (50 g) of soil sample was spiked with known amounts of CY. The extraction of pyrethroids in soil samples using *n*-hexane is reported in the literature [16, 17], so the solvent *n*-hexane was chosen for the extraction. Spiked soil samples were extracted twice with 50 mL of hexane and the organic layer was

Table 3. Recoveries of cyfluthrin, pure compound, and Baygon formulation added to tap-water and well-water samples.

Sample type	Amount added (mg)	Average amount[a] found (mg) ± SD	Average recovery (%)
Tap water spiked with pure compound	5.0	4.70 ± 0.035	94.00
	10.0	9.75 ± 0.087	97.50
Tap water spiked with formulation	5.0	4.80 ± 0.045	96.00
	10.0	9.29 ± 0.11	92.90
Well water spiked with pure compound	5.0	4.68 ± 0.027	93.60
	10.0	9.30 ± 0.024	93.00
Well water spiked with formulation	5.0	4.60 ± 0.10	92.00
	10.0	9.52 ± 0.035	95.20

[a] Each value is an average of three determinations.

separated by centrifugation. Then, the liquid fractions were mixed with 100 mL of water and a few millilitres of saturated sodium chloride. The extraction was done twice with 50 mL of acetone water (1 : 1), the extract was evaporated to dryness using a rotatory vaccum evaporator. The residue was dissolved in methanol and subjected to polarography. Recoveries of cyfluthrin from soils were given in table 2.

4.4 *Determination of cyfluthrin in water samples*

A 1000 mL water sample (well, tap) was spiked with a known amount of CY pure compound and formulation (Baygon), and shaken for few minutes. The solution was passed through a Whatman Nylon® membrane filter (0.45 μm size). Then, the filtrate was passed through a sep-pak C_{18} cartridge previously activated with 10 mL of acetonitrile and 5 mL of deionized water. Elution was carried out with 10 mL of acetonitrile and filtered through anhydrous sodium sulphate. The organic phase was evaporated to dryness in a rotatory vaccum evaporator, and the residue was dissolved in methanol, which was added to the cell containing buffer. The results obtained are listed in table 3.

5. Interference studies

The effect of the presence of other insecticides on the DPP signal such as propoxur, phoxim, and chlorpyrifos, which are usually used along with the analyte, has been tested. Propoxur is not electroactive. Phoxim and chlorpyrifos gives signals at −0.3 V and −1.1 V, which are said to not interfere with the analyte signal under the experimental conditions. Interference of humic acid, which is the most water-soluble organic component, is also studied. Under the experimental conditions, it did not produce any change in the recoveries of cyfluthrin, even if 40-fold excess was added.

6. Conclusions

It has been concluded that the electrochemical method developed does not involve the elaborate cleanup procedures required with the other methods and provides an accurate

and precise technique for the selective determination of CY in formulations, grains, soils, and water samples. The analytical results obtained by DPP in cyfluthrin formulation are in good agreement with the chromatographic method. This method might be an alternative to the chromatographic techniques.

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References

[1] G. Best. *Pesticides, Developments, Impacts and Controls*, The Royal Society of Chemistry, Cambridge (1995).
[2] J.H. Davies. In *The Pyrethroid Insecticides*, J.P. Leahey (Ed.), pp. 1–41, Taylor & Francis, London (1985).
[3] H.C. Oudou, R.M. Alonso, R.M. Jimenez. *Electroanalysis*, **13**, 72 (2001).
[4] D.C. Coomber, D.J. Tucker, A.M. Bond. *J. Electroanal. Chem.*, **10**, 163 (1998).
[5] D.C. Coomber, D.J. Tucker, A.M. Bond. *J. Electronal. Chem.*, **430**, 215 (1997).
[6] D.C. Coomber, D.J. Tucker, A.M. Bond. *J. Electronal. Chem.*, **426**, 63 (1997).
[7] D.C. Coomber, D.J. Tucker. *Anal. Chem.*, **68**, 1267 (1996).
[8] G.V. Subba Reddy, S.J. Reddy. *Talanta*, **44**, 627 (1997).
[9] T. Shono, J. Terauchi, K. Kitayama, Y. Tameshima, Y. Matsumura. *Tetrahedron*, **48**, 8253 (1992).
[10] J. Volke, A.M. Kardos. *Coll. Czech. Comm.*, **33**, 2560 (1968).
[11] P.G. Arapakos, M.K. Scott. *Tetrahedron Lett.*, **16**, 1975 (1968).
[12] G. Corbini, C. Biondi, D. Proietti, E. Dreassi, P. Corti. *Analyst*, **118**, 183 (1993).
[13] M. Sreedhar, J. Damodar, N.V.V. Jyothi, S. Jayarama Reddy. *Bull. Chem. Soc. Jpn.*, **73**, 2477 (2000).
[14] T. De Vries, J.L. Kroon. *J. Am. Chem. Soc.*, **75**, 2484 (1953).
[15] G. Madhavi, P.R.K. Reddy, S.J. Reddy. *Bull. Electrochem.*, **11**, 490 (1995).
[16] S. Babic, M. Petrovic, M. Kastelan-Macan. *J. Chromatogr. A*, **82**, 3 (1998).
[17] M.M. Galera, J.L. Martinez Vidal, A.G. Frenich, M.D. Gil Garcia. *J. Chromatogr. A*, **727**, 39 (1996).