STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LV, 1, 2010

DETERMINATION OF AROMATIC AMINES AND PHENOLS BY KINETIC METHODS BASED ON LANDOLT EFFECT

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ABSTRACT. A simple kinetic method for the determination of aniline (and substituted anilines) and phenols in water has been set up. A Landolt type system has been employed, using the hydrogen peroxide - bromide reaction in acidic media, with aniline as a trap for bromine. The course of the reaction was followed potentiometrically. The plot of potential versus reaction time exhibits an inflexion point either in presence or absence of the analyte. It is similar to a titration curve, exhibiting a delay on the abscissa. The value of the difference Δt between end-point times for the sample and the blank is proportional to the concentration of the trapping agent. According to the initial rate method in kinetically based analytical determinations, it represents the base of calibration. The best operating conditions regarding ionic strength, pH, concentration range of reagents and temperature have been established. The method was checked for mixtures of anilines or aniline and phenol. Additive effects were found. No discrimination among individual components is possible by this method. Depending on the analyte, detection limits were in the range of 1.7 - 52 $\mu g \cdot L^{-1}$. Copper and iron ions interfere in the determination only at large concentrations.

Keywords: *kinetic methods, phenols, aromatic amines*

INTRODUCTION

Phenols and aromatic amines are byproducts of large-scale production and use of man-made organics such as drugs, dyes, antioxidants, paper pulp and pesticides. They cause ecologically undesirable effects[1]. Most phenols and anilines exhibit different toxicities; hence their determination is very important for evaluating the total toxicity of an environmental sample.

Current methods for the determination of anilines include spectrophotometric methods [2-4], gas chromatography-mass spectroscopy techniques [5-7], high-performance chromatography [8-12] and sensors [13, 14].

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Generally, phenolic compounds are subjected to chromatographic separation before detection [15-17]. However, the separation takes time, and often requires pre-concentration. In addition, the equipment is expensive and usually is not portable. Many biosensors have been developed in the past for phenol determination [18-25].

This paper shows that aromatic amines and phenols can be determined bromometrically in water samples, with bromine generated *in situ* by a redox reaction. Many such brominations of activated aromatic compounds use various bromides and oxidizing agents (NH_4Br–H_2O_2 [26], *NaBr*–Oxone ($KHSO_5$–$KHSO_4$) [27], *HBr*–H_2O_2 [28, 29], *LiBr*–Cerium ammonium nitrate [30]) or even heterogeneous catalysis [31, 32].

The proposed kinetic method is based on the following two formal reactions:

$$H_2O_2 + 2Br^- + 2H^+ \xrightarrow{k_1} Br_2 + 2H_2O \quad (1)$$

$$XC_6H_4NH_2 + Br_2 \xrightarrow{k_2} XC_6H_3BrNH_2 + H^+ + Br^- \quad (2)$$

Reaction (2) can also be written with phenols. The bromination of the first-brominated compound can continue to second and/or third bromination. This type of bromination has been employed for synthetic purposes by using H_2O_2 and NH_4Br [26]. The rate constant for bromination reaction (2) is larger than that of reaction (1), where the brominating agent is formed, while the oxidation of aniline or phenols by hydrogen peroxide under the employed experimental conditions takes place slower as compared to process (1). Although further bromination takes place in consecutive steps, the substitution reactions are relatively rapid as compared to the brominating agent generation. Therefore, the couple of reactions (1) and (2) resemble a Landolt-type system.

The concentration of bromine is quite low, so that a steady-state is reached that depends on the nature of phenol or aniline. Different reactivity of aromatic amines or phenols towards bromine causes quite different steady-state concentration for this species. Under these steady-state conditions, the rate of nuclear bromination is independent of the substrate concentration, but depends on the nature of these species and the number of bromination steps. The overall stoichiometry for bromination of phenol molecules in a mixture of hydrogen peroxide - bromide ions in acidic media is given by:

$$3H_2O_2 + 3Br^- + 3H^+ + C_6H_5OH \xrightarrow{k} C_6H_2Br_3OH + 6H_2O \quad (3)$$

It was determined experimentally, by using mixtures with increasing ratio of bromine/phenol, that tri-bromination has taken place. These findings confirmed previous research [33]. The same tri-bromination occurs with aniline. As shown above, the rate of nuclear bromination depends primarily on the nature, but not on the concentration of the analyte. The electrophyle generation rate depends upon the H_2O_2, Br^- and H^+ concentrations [34].

RESULTS AND DISCUSSION

Figure 1a shows the evolution of electromotive force *vs* reaction time for kinetic runs of the blank and in the presence of *para*-toluidine and 3-aminobenzenesulfonic acid.

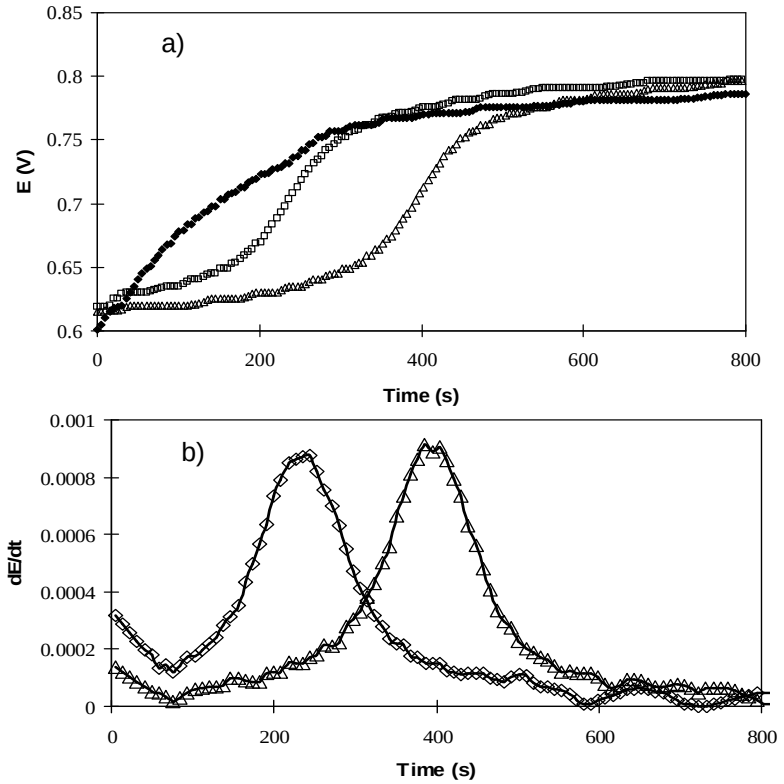

Figure 1. Electromotive force *vs* reaction time (a) and dE/dt (b) plots obtained in the determination of 0 (■), $2x10^{-5}$ $mol.L^{-1}$ *para*-toluidine (◇) and 3-aminobenzenesulfonic acid (△). Other experimental conditions are described under Procedures.

The graph exhibits an inflexion point and has the shape of a titration curve. The so-called “titration agent” is generated in the reaction mixture at a well-established rate. Therefore, the abscissa is time instead of “titration agent volume”. The end-point is considered to correspond to the inflection point on the curve. The time value at the inflexion is determined by derivation of the recorded curve (see Figure 1b). In fact, the complete consumption of the aromatic amine does not correspond to the inflection point, but to the moment at which the electromotive force increases steeply. This corresponds to the extrapolation to the abscissa of the linear increase of E values around the

inflection point. It should be mentioned that the formation of bromine in the absence of the trapping agent (blank probe) is not instantaneous. It generates a similar curve. However, the inflection point is more precisely determined by derivation of the curves. Therefore, we have chosen this approach. The difference $\Delta t = t - t_0$ is proportional to the amount of pollutant in the mixture. The values t_0 and t stand for the end-point times of a reaction mixture in the absence and in the presence of the analyte, respectively. Because the indicator reaction behaves as a Landolt-type system, the reciprocal of Δt is directly related to the value of the rate. According to the initial rate method in kinetically based analytical determinations, the base of calibration is the plots Δt *vs* pollutant concentration.

Optimisation of conditions. To achieve the maximum possible sensitivity with the proposed kinetic method, we searched for the effect of a number of parameters such as pH, concentration of reactants, conversion of hydrogen peroxide and temperature. The quest for the best condition was carried out with respect to the determination of 3-aminobenzensulphonic acid and of phenol.

The effect of the H^+ concentration on the reaction rate is shown in Fig. 2a. Hydrogen ions affect the Landolt- type system, namely the rate of bromine generation. The shape of the curves is similar either in the presence or in absence of amines. First-order dependence with respect to the hydrogen ion has been confirmed by our data, because of the linearity of graphs in Figure 2a. From the point of view of the ionic strength (high enough to cover any contribution by an unknown sample) and the convenience of reaction rate determination the value of 0.1 mole·L^{-1} was chosen for further measurements.

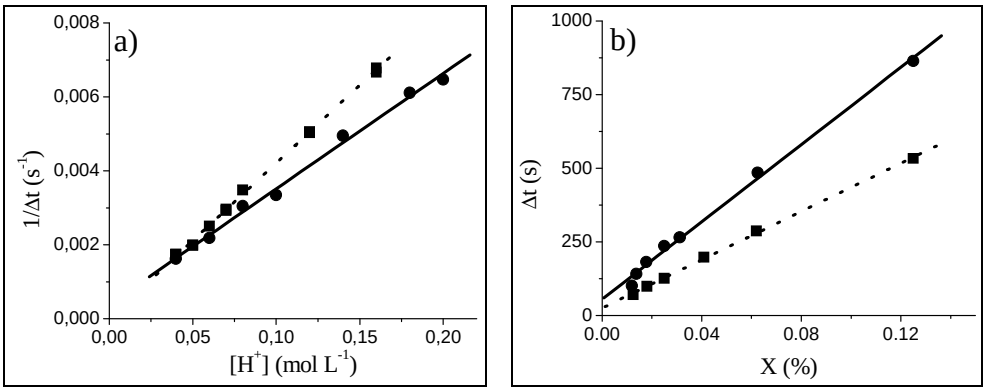

Figure 2. Influence of (a) $[H^+]$ and (b) conversion of H_2O_2 on kinetic determination of $2x10^{-5}$ mol.L^{-1} phenol (■) and aminobenzensulphonic acid (●). Other experimental conditions are described under Procedures.

The conversion of hydrogen peroxide is defined by:

$$X = \frac{[H_2O_2]_0 - [H_2O_2]_{cont}}{[H_2O_2]_0} = \frac{\Delta[H_2O_2]}{[H_2O_2]_0} = \frac{[analyte]_0}{[H_2O_2]_0} \quad (4)$$

The effect of the conversion on the reaction rate at a 3-aminobenzensulphonic acid and phenol concentration of $2x10^{-5}$ mole·L^{-1} is illustrated in Figure 2b. At low conversions, the end-point time is quite short to be precisely determined. At higher values, it is too long and the concentration of H_2O_2 smaller that of the start of the reaction. This is caused by the H_2O_2 consumption by bromide and by self-decomposition. Moreover, the initial rate method cannot be used at large consumption [36]. A compromise should be made. We have chosen a value of 0.025 (2.5 %). It ensures practically a constant rate within this initial part of the reaction. The concentrations of H^+, H_2O_2 and Br^- are almost constant.

The effect of temperature upon the reaction rate was examined in the range of 293–318 K. As expected, an Arrhenius-type dependence was observed. At higher values of temperatures, the decomposition of H_2O_2 becomes more important. A value of 298 K seems to be convenient for analytic measurements, either for reasonable rates of the process or for the negligible rates of side reactions.

Calibration curves. The electromotive force *vs* time curves recorded for different amounts of pollutant were analysed by the initial-rate method. Five aromatic amines: aniline, *para*-aminophenol, *para*-toluidine, 3-aminobenzensulphonic acid and *para*-iodoaniline and five phenols: phenol, resorcine, hydroquinone, *orto*-cresole and *β*-naphtole were examined. Data relevant for calibration graphs, covering the concentration range of two orders of magnitude (10^{-6} – 10^{-5} mol·L^{-1}), are summarised in Table 1. The detection limit was computed as recommended by IUPAC. ***R*** stands for the correlation factor.

The sensitivity, defined as the slope of the calibration lines (see Table 1), is good and depends on the nature of the analyte. The precision of the proposed method was checked on seven samples containing $2.0 \cdot 10^{-5}$ mol.L^{-1} phenol. The relative standard deviation was 3.2 %.

Effects of interfering species. The interfering effect of some metal ions and organic compounds associated with pollutants in wastewater was studied. The results are summarised in Table 2 for determination of phenol.

The following ions do not modify the rate of electrophile generation: Zn(II), Cd(II), Ni(II), Mo(VI), V(V), Fe(III), Cu(II). Their effect upon the amine determination is negligible. However, we noticed that copper ion interferes in reaction at relatively large concentrations. Cu(II) has a catalytic effect upon the decomposition of hydrogen peroxide and possibly on the oxidation of bromide by hydrogen peroxide.

Table 1. Features of calibration graphs for the determination of some aromatic compounds

Analyte	**Linear regression** Δt = end-point time (s); C = molar concentration (mole·L^{-1})	**R/ nr. points**	**Detection limit·10^7 (mol.L^{-1})**
Amines			
Aniline	$\Delta t = (-0.4 \pm 9.5) + (179 \pm 8) \cdot 10^6 \cdot C$	0.995/12	0.1
3-Aminobenzen-sulphonic acid	$\Delta t = (11 \pm 6.2) + (12.1 \pm 0.2) \cdot 10^6 \cdot C$	0.999/9	1.6
para-Amino phenol	$\Delta t = (16 \pm 26) + (54.7 \pm 0.5) \cdot 10^6 \cdot C$	0.999/9	0.4
para-Toluidine	$\Delta t = (17.2 \pm 13) + (11.6 \pm 0.3) \cdot 10^6 \cdot C$	0.999/9	1.7
para-Iodaniline	$\Delta t = (2.8 \pm 3.4) + (14.8 \pm 0.3) \cdot 10^6 \cdot C$	0.999/11	1.3
Phenols			
Phenol	$\Delta t = (-3.1 \pm 3.1) + (8.5 \pm 0.2) \cdot 10^6 \cdot C$	0.998/18	2.3
ortho-Cresole	$\Delta t = (-0.9 \pm 2.3) + (5.7 \pm 0.2) \cdot 10^6 \cdot C$	0.998/11	3.5
Hidroquinone	$\Delta t = (-0.9 \pm 2.3) + (5.5 \pm 0.2) \cdot 10^6 \cdot C$	0.999/9	3.6
Resorcine	$\Delta t = (-1.2 \pm 4.8) + (20.2 \pm 0.4) \cdot 10^6 \cdot C$	0.999/11	0.9
β-Naphtol	$\Delta t = (0.4 \pm 3.9) + (0.86 \pm 0.06) \cdot 10^6 \cdot C$	0.995/7	23.0

Table 2. Tolerance limit for various organic compounds and ions on the determination of 2x10^{-5} mol.L^{-1} phenol

Interfering species	**Tolerance limit ratio (mole/mole)**
oxalic acid, isopropylic acid, ethanol, methanol	400*
Zn(II), Cd(II), Ni(II), Mo(VI), V(V), KCl, EDTA	200*
Fe(III), Cu(II)	90
Vitamin B_{12}	100*
cysteine, methionine, ascorbic acid, acetylsalicylic acid, paracetamol, vitamin B_6, vitamin B_2	1

**maximum limit tested*

The most serious interference in these analyses was caused by: *B* vitamins, acetylsalicylic acid and ascorbic acid. These react with bromine in the same manner as the aromatic amines and phenols.

All aromatic amines and all phenols employed in the study react similarly. Therefore, no discrimination among them is possible in mixtures. This constitutes a drawback of the method.

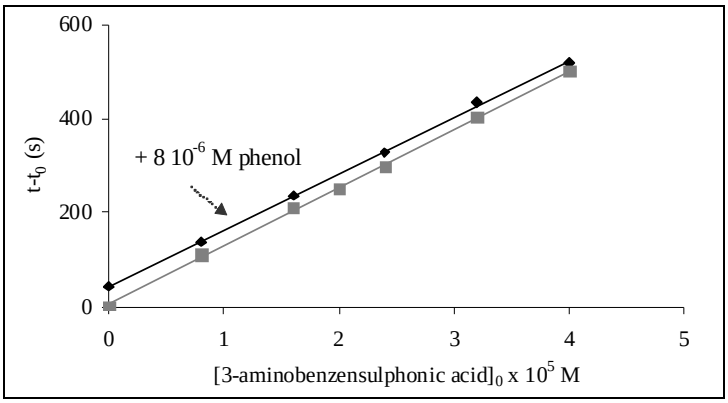

Figure 3. Calibration line in the absence and presence of a constant concentration of phenol ($8x10^{-6}$ $mol.L^{-1}$). Other experimental conditions are described under Procedures.

Nevertheless, a mixture of two analytes can be determined as a sum. If a known and constant concentration of phenol and increasing concentrations of 3-aminobennzensulfonic acid are used in calibration, the obtained calibration lines are parallel. This is illustrated in Figure 3 and indicates the additivity of the end-point times. The same behaviour has been observed for *p-t*oluidine and 3-aminobenzensulfonic acid mixtures.

Table 3. Recovery of aniline added or determined concentration in waste-water

Sample provenience	$[aniline]_0 \times 10^6$ (M)			Recovery (%)
	added	Standard Method [37]	Kinetic method	
River water with added aniline	1.58 4.17 8.35	1.60 4.10 8.32	1.52 4.15 8.28	101.3/96.2 98.3/99.5 99.6/99.1
Several samples of wastewater		7.1 3.5 1.7 0.60 1.30 2.20 2.30 3.40	7.22 3.61 1.62 0.63 1.26 2.15 2.29 3.41	100.7 103.1 95.3 105.0 96.9 97.7 99.6 100.3

Testing on some real samples. The aniline content in several samples of waste-water from S.C. Sinteza Oradea S.A. was determined by our technique. Results were compared to those obtained by means of the Romanian Standard for determination of aniline in surface and waste-waters. This is an equilibrium

spectrophotometrical method and relies on the oxidative coupling of amine with phenol in the presence of chloramine T to yield an indophenol dye [37]. Some measurements have been carried out by adding known amounts of aniline to previously analysed river water samples. These contained micromolar amounts of: Fe(II), Fe(III), Cu(II) and Mn(II), repectively. The recoveries were calculated relative to this method and the results are presented in Table 3. They correspond to mean values of at least three replicate experiments and range between 95% and 105 %, proving the proposed kinetic method is reliable.

EXPERIMENTAL SECTION

Reagents. Analytical-grade and commercially available chemicals were used without further purification, with the exception of phenol. Solutions were prepared first in deionised and four-distilled water and, after the study of various effects, only in twice-distilled water. Precautions taken at the beginning of the study, concerning the interference of metal ions, proved to be not entirely necessary. Stock solutions (1.0×10^{-3} mole·L^{-1}) were prepared from the aromatic amines and phenol in ethanol. The phenol solution was prepared from freshly purified stuff (distillation under low pressure; m.p. 40.5 – 41.5^{o}C).

Perchloric acid (0.5 mole·L^{-1}) and potassium bromide (0.5 mole·L^{-1}) were prepared in de-ionised and twice-distilled water. Hydrogen peroxide solution ($8.0 \cdot 10^{-2}$ mol·L^{-1}) was freshly prepared before each set of runs and standardised by common titration with permanganate.

Apparatus. The instrumental set-up was described in detail previously [35]. It consists of a temperature controlled reaction vessel. The measuring electrode was a platinum plate, the electromotive force being measured against a saturated calomel electrode by means of a potentiometer (Digitronix, DXP 2040). The latter is connected to a 32-bit Hewlett-Packard analogue-digital converter and a DTK computer.

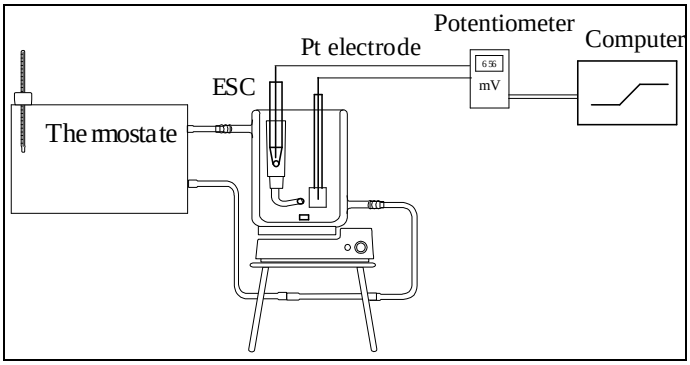

Figure 4. Experimental device

Procedure. Various aliquots of standard aniline or phenol solution, 5.0 mL of 0.5 mole·L^{-1} $HClO_4$ and 5.0 mL of 0.5 mole·L^{-1} *KBr* were placed in a 50-mL reaction vessel and accurately diluted to 20 mL. The reaction was initiated by rapid addition of 5 mL solution of hydrogen peroxide $8.0x10^{-2}$ mole·$L^{-1}$by means of a syringe. The progress of reaction was monitored potentiometrically and kinetic data (electromotive force *vs* reaction time) were collected and processed. Each measurement was carried out at least in triplicate.

CONCLUSIONS

The proposed method is simple, cheap and permits the determination of low concentrations of aromatic amines or phenols if only one species is present in the sample. If it contains more compounds, the total concentration of the pollutants can be determined as a sum. Depending on the analyte, detection limits range between 1.7 and 52 μg·L^{-1}. Data acquisition by means of a personal computer facilitates data collection and processing. Transition metals do not interfere at concentration levels usually encountered in surface or wastewater.

ACKNOWLEDGEMENT

Financial support of Romanian National University Research Council (CNCSIS) is gratefully acknowledged by the authors.

REFERENCES

1. S. Canofeni, S. Disario, J. Mela, R. Pilloton, *Anal. Lett.,* **1994**, *27*, 1659.
2. N. A. Zatar, A. Z. Abu-Zuhri, A. A. Abu-Shaweesh, *Talanta,* **1998**, *47,* 883.
3. A. Labudzinska, K. Gorczynska, *Analyst,* **1994**,*119*, 1195.
4. L. Copolovici, L. Baldea, *Anal. Bioanal. Chem.,* **2002***, 374*, 13.
5. K. J. Chia, S. D. Huang, *J. Chromatogr. A,* **2006**, 1103, 158.
6. M. Akyuz, S. Atu, *J. Chromatogr. A,* **2006***, 1129*, 88.
7. C. H. Deng, N. Li, L. Wang, X. M. Zhang, *J. Chromatogr. A,* **2006**, 1131.
8. L. Cardenes, A. Martin-Calero, J. H. Ayala, V. Gonzalez, A. M. Afonso, *Anal. Lett.,* **2006**, *39*, 405.
9. X. N. Cao, J. H. Li, H. H. Xu, J. R. Zhan, L. Lin, K. Yamamoto, L. T. Jin, *Chromatographia,* **2004**, *59*, 16.
10. J. W. Blythe, A. Heitz, C. A. Joll, R. I. Kagi, *J. Chromatogr. A,* **2006***, 1102*, 73.
11. M. I. Evgen'ev, I. I. Evgen'eva, F. S. Levinson, E. A. Ermolaeva, Y. R. Valitova, *J Anal. Chem,* **2006***, 61*, 133.

12. Y. Zhu, M. H. Wang, H. Y. Du, F. Wang, S. F. Mou, P. R. Haddad, J. *Chromatogr. A,* **2002**, *956*, 215.
13. M. Wimmerova, L. Macholan, *Biosens. Bioelectron.,* **1999***, 14,* 695.
14. A. Ferancova, E. Korgova, J. Labuda, J. Zima, J. Barek, *Electroanal,* **2002**, *14*, 1668.
15. M. Kladi, M. Dassenakis, M. Scoullos, N. Psaroudakis, *Fresen*. *Environ. Bull.,* **2006**, *15*, 1003.
16. A. Asan, I. Isildak, *J. Chromatogr. A,* **2003**, *988*, 145.
17. M. S. Zhang, A. M. Wang, *Chinese Anal. Chem.,* **1999**, *27*, 63.
18. S. L. Mu, *Biosens. Bioelectron*., **2006**, *21*, 1237.
19. Z. H. Dai, X. X. Xu, L. Wu, H. X. Ju, *Electroanal.,* **2005**, *17,* 1571.
20. N. Li, M. H. Xue, H. Yao, J. J. Zhu, *Anal. Bioanal. Chem.,* **2005**, *383*, 1127.
21. Q. Zhao, L. H. Guan, Z. N. Gu, Q. K. Zhuang, *Electroanal.,* **2005**, *17,* 85.
22. H. H. Yu, S. Q. Liu, H. X. Ju, *Biosens. Bioelectron.,* **2003**, *19*, 509.
23. J. Kulys, R. Vidziunaite, *Biosens. Bioelectron.,* **2003***, 18*, 319.
24. S. C. Chang, K. Rawson, C. J. McNeil, *Biosens. Bioelectron.,* **2002**, *17*, 1015.
25. Y. I. Korenman, S. A. Tunikova, N. V. Belskikh, M. Bastic, L. Rajakovic, *J. Anal. Che*m., **1997**, *52*, 278.
26. K. Mohan, N. Narender, P. Srinivasan, S. J. Kulkarni, K. V. Raghavan, *Synthetic Commun.,* **2004**, *34*, 2143.
27. C. K. Lee, B. S. Koo, Y. S. Lee, H. K. Cho, K. J. Lee, B. *Kor. Chem. Soc.,* **2002**, *23*, 1667.
28. N. B. Barhate, A. S. Gajare, R. D. Wakharkar, A. V. Bedekar, *Tetrahedron Lett.,* **1998**, *39*, 6349.
29. R. Neumann, I. Assael, *Chem. Commun.,***1988**, 1285.
30. S. C. Roy, C. Guin, K. K. Rana, G. Maiti, *Tetrahedron Lett*., **2001**, *42*, 6941.
31. T. Esakkidurai, M. Kumarraja, K. Pitchumani, *Catal. Lett.,* **2004**, *92*, 169.
32. D. P. Das, K. Parida, *Catal. Commun*., **2006***, 7,* 68.
33. A. W. Francis, A. J. Hill, *J. Am. Chem. Soc,* **1924**, *45*, 2498.
34. S. U. Kreingold, L. V. Lavrelashvili, I. M. Nelen, *J. Anal. Chem. USSR,* **1982**, *37*, 1441.
35. S. Bungau, I. Baldea, L. Copolovici, *Rev. Chim. Bucharest,* **2003**, 54, 213.
36. H. A. Mottola, "Kinetic aspects of analytical chemistry", (Vol. 96 of the Series "Chemical Analysis"), John Wiley&Sons, New-York, **1988**, pg. 20; A. Csavdári, "Catalytic Kinetic Methods in Analytical Chemistry. Principles and applications", **2008**, Editura MEGA, Cluj-Napoca.
37. ***, STAS 8507-70, *"*Eaux de surface et eaux usees. Dosage de l'aniline"; V. G. Amelin *J. Anal. Chem.*, **2002**, *57*, 733; J. F. Van Bocxlaer, K. M. Clauwaert, W. E. Lambert and A. P. De Leenheer, *Clin. Chem*., **1997**, *43*, 627.