ISSN-1680-9955

Pak. J. Anal. Envir. Chem. Vol. 7, No. 1, (2006) 1 – 7

# Principles and Analytical Applications of Phase-Transfer Catalysis

YIANNIS C. FIAMEGOS, **CONSTANTINE D. STALIKAS*** AND MILTIADIS I. KARAYANNIS
*Laboratory of Analytical Chemistry, Department of Chemistry, University of Ioannina, Ioannina 451 10, Greece*

**E-mail: cstalika@cc.uoi.gr*

**Abstract**

Phase-transfer catalysis (PTC) has been widely used for the synthesis of organic compounds for more than three decades. The scope and mechanistic features of PTC have been the aim of numerous studies. This review is approaching the subject by focusing on the extraction-preconcentration-derivatization prior to analysis, reporting recent progress made. Moreover an attempt is made to approach the salient aspects of PTC modes including a brief review of mechanistic pathways and kinetics pointing out the potency of PTC in analytical chemistry. Optimization guidelines for PTC-based analysis are given with respect to all parameters influencing the analytical method under development, highlighting the capabilities and limitations of PTC reactions.

**Keywords:** *phase-transfer catalysis, analytical applications.*

## Introduction

Isolation and preconcentration of analytes by liquid-liquid extraction is a rather popular sample pretreatment technique in trace analysis for the removal of interferences. Classical solvent exchange consists in bringing into contact two immiscible solvents such as water and an organic one transferring solutes from one liquid phase to the other.

Based on the assumption that a reaction between lipophilic and hydrophilic reactants is facilitated by enhancement of mutual solubility, the transfer of a solute between phases is crucial for the establishment of liquid-liquid distribution equilibria [1]. Thus, high transfer rate is required, which can be achieved by increasing the area of the interface [2]. Phase-Transfer Catalysis (PTC) is a well-known method of promoting reactions between reagents with opposite solubility preferences. In such systems each reactant is dissolved in the appropriate solvent. Commonly, the two solvents are immiscible to one another, and then a phase-transfer catalyst is added to facilitate the transport of one reactant into the other phase.

*Author for Correspondence

By means of the catalytic step, the enhanced reactivity between the ionic species leads to increase of the rate of the desired reaction. The unique characteristics of phase-transfer catalysis are essential for developing analytical applications and thus PTC has been implemented as a tool for the simultaneous extraction, preconcentration and derivatization in the analysis of certain organic and inorganic compounds.

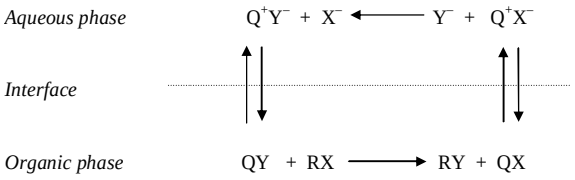
The multiple aspects of PTC in analytical chemistry can be considered in a general-purpose review, but the aim of this brief one is twofold: Firstly to present certain developed analytical applications based on PTC. Secondly, to present the theoretical background of the overall process giving in short, some kinetic and mechanistic properties of the most common applications published.

### Historical Development and Principles

In the seventies, PTC became a method for overcoming problems of mutual solubility with simultaneous activation of anions [3] and was

originally employed for reactions between ionic compounds and organic, water insoluble substances in solvents of low polarity [4]. Later, PTC included extraction of cations or even neutral molecules from one phase into another by means of the catalyst. 'Inverse' phase-transfer-catalyzed extraction of species into the water phase was also studied using partially water-soluble pyridines [5,6].

The mechanism of PTC reaction was first proposed in 1971 [7]. According to Starks' original work, a quaternary ammonium halide dissolved in the aqueous phase ($Q^+X^-$) undergoes anion exchange with the anion of the reactant dissolved in the aqueous solution. The ion-pair formed ($Q^+Y^-$) can cross the liquid-liquid interface due to its lipophilic nature and diffuses from the interface into the organic phase, this step being the "phase-transfer". In the organic phase, the anion of the ion-pair being quite nucleophilic undergoes a nucleophilic substitution reaction with the organic reagent forming the desired product (RY). The catalyst subsequently returns to the aqueous phase and the cycle continues. An overview of PTC reactions is given in the scheme bellow:




A prerequisite for a substance to function as a PT-Catalyst is to form ion-pairs soluble in the organic phase and to be transferred in a highly active state [8,9]. High extraction constant values for the ion-pair are obtained as lipophilic chain of quaternary onium cations is elongated [10,11].

An important issue that dictates reactivity is the *solvation*. The amount of water that is co-extracted with the ion-pair into the organic phase may interfere with the desired reaction. Reducing the hydration sphere of the anion or using solid-liquid PTC conditions can overcome this drawback. As this mode presupposes water-free reactions, it found few followers in the field of analytical chemistry. Such applications are the determination of carboxylic acids [12], the quantitation of acidic tryptophan metabolites [13], the determination of 5-fluorouracil in plasma [14] and uracil in DNA [15], the analysis of long chain fatty acids [16] and the simultaneous determination of trace levels of haloacetic acids in biological samples as their pentafluorobenzyl derivatives [17].

Other mechanisms that can be considered as phase-transfer catalytic are:

1. **PTC of uncharged species:** complexation and transfer of uncharged protic species or metal salts into the organic medium as complexes of the phase -transfer agent [18].
2. **Electron-transfer catalysis** for Redox systems [19-22].
3. **metal ion-transfer** from aqueous solutions into water-immiscible ionic liquids containing neutral complexing agents [23].
4. **Pyrolytic alkylation process**, whereby thermal decomposition of a quaternary ammonium salt yields a volatile alkyl derivative in the heated injector of a gas chromatograph [22].

The PTC techniques have, in principle, been used in connection with separation analytical methods, with gas and liquid chromatography being the main applications. De Ruiter and Lingeman in the "Handbook of phase-transfer catalysis" provide significant reference on analysis by PTC [18]. It should be clear that only recent and significant analytical PTC derivatizations are included in this review article.

## Phase-Transfer Catalysis

Phase transfer catalysts can be either homogeneous (soluble in one or both solvents) or heterogeneous.

### *Homogenous PTC applications*

Quaternary ammonium, phosphonium and arsonium salts (generally termed "onium" salts) provide a source of singly charged lipophilic cations. In general, catalyst efficiency is influenced by the large number of carbon atoms (high lipophilicity) and the symmetry of the carbon atom chains about the heteroatom.

Homogenous PTC is based on the mechanism described in paragraph 2 and according to this a number of applications have been developed.

Chlopyralid in soil samples, was analyzed by GC-MS after its reaction with tetrabutylammonium hydroxide [24]. Aliphatic alcohols were derivatized to dithiocarbonates and determined by capillary zone electrophoresis [25]. Alkylphenols were converted to their 4-tetrafluoropyridyl derivatives and analyzed with GC-MS [26]. Urine saliva and hair extracted smoke uptake parameters (thiocyanate, nicotine and cotinine) were determined with GC after their PTC pentafluorobenzylation [27]. Haloacetic acids have been methylated and analyzed by a static headspace GC-MS method [28] while organic acids were rapidly methylated and extracted using supercritical carbon dioxide containing methylation reagents and PTC [29, 30].

In this concept, PTC was used for the analysis of carboxylic acids [31-33] acidic herbicides [22,34], diuretics, urinary acidic moieties and buprenorfine [35-38], ethylene thiourea [39], sulphide, polysulphides, cyanide, and thiocyanate [40-43], nitrate, nitrite [44,45], methanol [46], iodide, cyanide, nitrite and thiocyanate [47,48], levorphanol [49], phenols [50], phenoxyacetic acids [51] and perfluorooctanoic acid [52].

The cryptates like Kryptofix 222, and the so-called "polypodes" [53] and "octopus molecules" [54,55] were not widly used as catalysts, because they are difficult to prepare and most of them are commercially unavailable.

Tertiary amines (e.g. triethylamine) can form *in situ* onium salts acting as PTCs. In this context, phenols [56] methamphetamine and amphetamine [57] were GC analyzed after derivatization with triethylamine. Additionally, phenylacetic acid in human plasma was determined by a PTC-based method [58], while a precolumn derivatization method with Nile Blue in the presence of 2-chloro-1-methylpyridinium iodide and triethylamine, as catalyst was used for the determination of acids.

***Heterogenous PTC applications***

PTCs linked to a polymer matrix are described as heterogenous catalysts [59]. Many materials have been developed in this context, some of them specialized to catalyze specific reactions [60-62]. In this case, the catalyst is bonded to a matrix forming a third immiscible solid phase between the organic and aqueous ones involving a swelling, mixing and diffusion during the reaction. Due to diffusion retardation, reactions with slow intrinsic reaction rates are much slower with a tri-phase catalyst than with its homogeneous counterpart [11,32]. On the other hand, the use of tri-phase PTC simplifies the removal of the catalyst after the reaction which can be re-used until they lose their mechanical stability [9,63,64]. In general, a polymer-supported catalyst consists of a hydrophobic polymer backbone solvated in the organic solvent and a hydrophilic part containing water and the nucleophile. In agreement to the extraction mechanism for homogenous PTC reactions, phase-transfer cycle in a tri-phase PTC consists of an ion-exchange step in the aqueous phase followed by the reaction in the organic-phase. A major difference between the two mechanisms is that in a tri-phase PTC system the catalyst movement is restricted and the organic and aqueous reagents must be brought to the catalyst cation. The catalyst structure and loading, the spacer chain, the polymer structure, the agitation and the swelling power of the solvent, the concentration of reactant, the type of the anion, the organic leaving group and the catalyst cation are some of the criteria that should be considered in tri-phase PTC.

Application of polymeric bonded PTC for the determination of cyanide, iodide, nitrite, sulphide and thiocyanate, led to easy layer separation and PTC-free injection of the sample into the chromatograph [65, 66].

Tributylbenzylammonium bromide was used for the determination of tetrahydroisoquinolines [67]. Cyanuric acid which is a highly polar, hydrophilic molecule was simultaneously extracted-preconcentrated and derivatized under tri-phase PTC conditions [64]. Anionic organic compounds in aqueous samples were analyzed by

extractive pentafluorob-enzylation using tri-*n*-butylmethylphosphonium salt [68].

Phenolates were also derivatized with considerable yields in a range of acidity (from thymol to pentachlorophenol) and polarity (from resorcinol to pentachlorophenol) [69].

Tri-phase PTC was also used for the determination of: carboxylic acids [70], 4-hydroxycoumarin anticoagulants [71], amino acids and peptides [72], dialkylphosphates, carboxylic acids and phenols [73], fluoroacetic acid and phenoxy acid herbicides [74], alkylmethylp-hosphonic acids [75], azide, cyanide and thiocyanate [76], phenolic acids and flavonoids [77].

***Kinetics and Interfacial Phenomena in PTC***

Small amounts of PT catalyst in extremely slow reactions between components existing in two immiscible phases are usually sufficient to accelerate them. This capability strongly depends on:

i) The distribution equilibrium of the PTC in the two phases,
ii) The mass-transfer rate between the imiscible phases and
iii) The reaction rate in the organic phase.

The distribution of quaternary salts and their surface activity near the interface between the two media is a critical factor for the reaction [78-80]. The interfacial area depends on the rate of stirring and affects the position of the extraction equilibrium of the ion-pairs [79]. Kinetics and mechanism in homogenous phase-transfer catalysis, under vigorous agitation conditions, have been reviewed [81]. The reaction rate strongly depends on the distribution ratio $D_{QY}$ as given below.

$$D_{QY} = \frac{[Q^+Y^-]_{org}}{[Y^-]} = K_{ex(QY)} \cdot [Q^+]$$

where $Q^+$ is the counter ion, $Y^-$ is the nucleophilic anion, $K_{ex(QY)}$ is the extraction constant and $D_{QY}$ is the distribution ratio of the ion-pair $Q^+Y^-$. From this equation is obvious that the distribution ratio depends on the concentration of $Q^+$ and the extraction constant, $K_{ex(QY)}$.

The reaction mixture requires a minimum stirring speed to achieve optimum phase contact. Under these conditions it is assumed that the phases are in equilibrium with each other.
In this vain, the rate of the overall reaction is controlled by the reaction in the organic phase which is a pseudo-first-order reaction [10].

$$\text{Rate} = k_{obs} [QY]_{org} ,$$

where $k_{obs}$ is the pseudo-first-order reaction rate constant.

The solvation of polar analytes by water molecules, in polar solvents affects the anionic reactivity significantly. Wu *et al* assessed the extraction behaviour of various quaternary salts in the presence of NaOH based on their respective distribution data from aqueous solution to dichloromethane or chlorobenzene [82].

In tri-phase PTC there are various parameters affecting the overall behaviour of the reaction [83-87]. Ion-exchange kinetics, mass transfer of reactants in the bulk aqueous and organic phases as well as diffusion of reactants within the catalyst are seriously considered. It is commonly suggested that the ion-exchange reaction is very fast and thus is always in equilibrium. As a result, the mass transfer of reactants, the intraparticle diffusion of reactants, and the intrinsic organic reaction rate at the active sites determines the reaction rate. Research studies have assumed that this kind of PTC reactions have as rate limiting step the intrinsic reaction rate at the catalyst's active sites [83,88,89]. The overall rate of reaction between an organic substrate RX and an inorganic nucleophile $Y^-$ to form organic product RY in the presence of tri-phase catalyst QX, depends on the concentrations of RX and $Q^+Y^-$:

$$\text{Rate} = k_{org} [RX]_{org} [Q^+Y^-]_s$$

where $[RX]_{org}$ is the concentration of the reactant in the organic phase and $[Q^+Y^-]_s$ the concentration of ion-pair (nucleophile) in the catalytic sites.

***Method Development***

Several factors affect the reaction rate and derivatization yield of simple PTC reactions like the one between an organic reagent and an analyte. These factors are: the structure of R groups, the activity of the leaving group, the nucleophilicity of the group analyte, the relative transfer efficiency of the analyte between phases, the organic solvent type, the reagent concentration, the agitation intensity and the temperature. In general, heterogenous PTC have a lower reactivity compared to their soluble analogs although there are specific reaction conditions under which the supported catalysts perform better than their soluble counterparts [9,64].

Optimization of the reaction conditions for the development of a PTC-based analytical method, include parameters such as pH, kind of solvent and catalyst, the concentration of the organic reagent, the phase ratio and volumes, the reaction time, the temperature and the agitation.
Compounds with more than one labile protons lead to the formation of several derivatives making the overall procedure more complicated. In this case, careful optimization of the reaction conditions is required in order to move the reaction to the desired products. Literature search shows that analysts can acquire good performance with economical and multiple-use instruments such as GC and HPLC by expedient sample extraction-derivatization-preconcentration.

Finally, of paramount importance are the study of interferences to the derivatization rate and the extent of conversion. Usually, interferences are associated with co-existing nucleophilic anions like $Cl^-$ which can be avoided by mercury(II) complexation and dilution [90].

## Conclusions

Method-development strategies usually discount analytical derivatization at the outset because of additional steps, excess of reagent and the concomitant potential for interferences. However, there are numerous examples where analytical derivatizations are called for to enhance sensitivity, selectivity, extraction efficiency and overall quality of the data. Improvements resulting from derivatization in instrumental methods are well known. The development of automated and/or miniaturized techniques in connection with the measuring analytical devices at hand, demonstrated that the concerns regarding extra steps and time requirements are not necessarily at issue. Derivatization of the analytes in a PTC system looks more advantageous than conventional techniques such as time-consuming extraction procedures. In the domain of analytical chemistry, PTC methods offer extraction-preconcentration and derivatization of analytes in one step increasing detection sensitivity. In this way, analysts can obtain high performance with economical and multiple-use instruments such as GC and HPLC. It can, therefore, be regarded a promising technique focussed on the analytical chemistry solution reactions.

## References


1. B. Tremillon, In: *Reactions in solutions. An applied analytical approach.* J. Wiley (Eds.), Chichester, (1997).
2. C. A. Bunton, In: *Surfactant Science Series*; M. Gratzel, K. Kalyanasundaram, Eds.; Marcel Dekker, Inc.: New York, Vol. 38 (1991).
3. E. V. Dehmlow, *Angew. Chem. Int. Ed. Eng*., 16 (1977) 493.
4. D. R. Knapp, In: *Analytical Derivatization Reactions*. J. Wiley (Eds.), New York, 1979.
5. C. -S. Kuo, J. -J. Jwo, *J. Org. Chem*., 57 (1992) 1991.
6. B. Boyer, A. Hambardzoumian, G. Lamaty, A. Leydet, J. -P. Roque, P. Bouchet, *New J. Chem*., 20 (1996) 985.
7. C. M. Starks, *J. Am. Chem. Soc*., 93 (1971) 195.
8. C. De Ruiter, R. Otten, U. Brinkman, R. Frei, *J. Chromatogr.*, 436 (1988) 429.
9. H. J. Glatzer, L. K. Doraiswamy, *Chem. Engin. Sci*., 55 (2000) 5149.
10. E. V. Dehmlow, S. S. Dehmlow, In: *Phase-Transfer Catalysis*, VCH: Weinheim and New York, (1993).
11. C. M. Starks, C. L. Liotta, M. Halpern, In: *Phase-Transfer Catalysis: Fundamentals, Applications and Industrial Perspectives*, Chapman & Hall, (1994).

12. A. Arbin, H. Brink, J. Vessman, *J. Chromatogr. A*, 196 (1980) 255.
13. D. B. Naritsin, B. R. L., S. P. Markey, *Anal. Chem.*, 67 (1995) 863.
14. K. Wang, M. Nano, T. Mulligen, E. D. Bush, R. W. Edom, *J. Am. Soc. Mass Spectrom.*, 9 (1998) 970.
15. J. Ren, A. Ulvik, H. Refsum, P. M. Ueland, *Anal. Chem.*, 74 (2002) 295.
16. C. Y. Lu, H. L. Wu, S. H. Chen, H. S. Kou, *Chromatographia*, 51 (2000) 315.
17. M. Jia, W. W. Wu, R. A. Yost, P. A. Chadik, P. W. Stacpoole, G. N. Henderson, *Anal. Chem.*, 75 (2003) 4065.
18. Y. Sasson, R. Neumann, In: *Handbook of Phase Transfer Catalysis*, Blackie Academic, Glasgow (1997).
19. G. Rothenberg, G. Barak, Y. Sasson, *Tetrahedron*, 55 (1999) 6301.
20. T. Endo, Y. Saotome, M. Okawara, *J. Am. Chem. Soc.*, 106 (1984) 1124.
21. K. K. Park, C. H. Oh, W. K. Joung, *Tetrahedron Lett.*, 34 (1993) 7445.
22. M. Rompa, E. Kremer, B. Zygmunt, *Anal. Bioanal. Chem.*, 377 (2003) 590.
23. M. P. Jensen, J. A. Dzielawa, P. Rickert, M.L. Dietz, *J. Am. Chem. Soc.*, 124 (2002) 10664.
24. S. Schutz, H. Vedder, R. -A. During, B. Weissbecker, H.E. Hummel, *J. Chromatogr. A*, 754 (1996) 265.
25. W. Lee, L. Liu, D. Lau, R. Chan, *Anal. Lett.*, 32 (1999) 1235.
26. M. Kojima, S. Tsunoi, M. Tanaka, *J. Chromatogr. A*, 984 (2003) 237.
27. J. Torano, H. Van Kan, Analyst, 128 (2003) 838.
28. P. L. Neitzel, W. Walther, W. Nestler, *Fresenius J. Anal. Chem.*, 361 (1998) 318.
29. V. Lopes-Avila, N. S. Dodhiwala, W. F. Beckert, *J. Agric. Food Chem.*, 41 (1993) 2038.
30. M. Y. Croft, E. J. Murby, R. J. Wells, *Anal. Chem.*, 66 (1994) 4459.
31. Y. L'emeillat, J. F. Menez, F. Berthou, L. Bardou, *J. Chromatogr. A*, 206 (1981) 89.
32. M. K. Bicking, N. A. Adinolfe, *J. Chromatogr. Sci.*, 23 (1985) 348.
33. S. Jacobsson, A. Larsson, A. Arbin, A. Hagman, *J. Chromatogr.*, 447 (1988) 329.
34. H. D. Meiring, G. den Engelsman, A. P. J. M. de Jong, *J. Chromatogr. A*, 644 (1993) 357.
35. A. M. Lisi, G. J. Trout, R. Kazlauskas, *J. Chromatogr. B*, 563 (1991) 257.
36. A. M. Lisi, R. Kazlauskas, G. J. Trout, *J. Chromatogr. B*, 581 (1992) 57.
37. A. M. Lisi, R. Kazlauskas, G. J. Trout, *J. Chromatogr. B*, 617 (1993) 265.
38. A. M. Lisi, R. Kazlauskas, G. J. Trout, *J. Chromatogr. B*, 692 (1997) 67.
39. H. D. Meiring, A. P. J. M. de Jong, *J. Chromatogr. A*, 683 (1994) 157.
40. S. Kage, T. Nagata, K. Kimura, K. Kudo, *J. Forensic Sci.*, 33 (1988) 217.
41. S. Kage, T. Nagata, K. Kudo, *J. Chromatogr. B*, 564 (1991) 163.
42. S. Kage, T. Nagata, K. Kudo, *J. Chromatogr. B*, 675 (1996) 27.
43. R. Hyspler, A. Ticha, M. Indrova, Z. Zadak, L. Hysplerova, J. Gasparic, J. Churacek, *J. Chromatogr. B*, 770 (2002) 255.
44. S. Kage, K. Kudo, N. Ikeda, *J. Chromatogr. B*, 742 (2000) 363.
45. S. Kage, K. Kudo, N. Ikeda, *J. Anal. Toxicol.*, 26 (2002) 320.
46. S. -H. Chen, H. -L. Wu, C. -H. Yen, S. -M. Wu, S. -J. Lin, H. -S. Kou, *J. Chromatogr. A*, 799 (1998) 93.
47. S. -J. Lin, H. -L. Wu, C. -Y. Lin, *Anal. Chim. Acta*, 386 (1999) 113.
48. F. Lin, H. Wu, H. Kou, S. Lin, *J. Agric. Food Chem.*, 51 (2003) 867.
49. E. T. Everhart, P. Shwonek, P. Jacob III, M. C. Rowbotham, R. T. Jones, *J. Chromatogr. B*, 729 (1999) 173.
50. F. Feng, B. Uno, M. Goto, Z. Zhang, D. An, *J. Chromatogr. Sci*, 41 (2003) 337.
51. M. I. Catalina, J. Dalluge, R. J. J. Vreuls, U. A. T. Brinkman, *J. Chromatogr. A*, 877 (2000) 153.
52. Y. Ylinen, H. Hanhijarvi, P. Peura, O. Ramo, *Arch. Environ. Contam. Toxicol.*, 6 (1985) 713.
53. B. Dietrich, J. M. Lehn, *Tetrahedron Lett.*, 14 (1973) 1225.
54. E. Nomura, H. Taniguchi, K. Kawaguchi, Y. Otsuji, *J. Org. Chem.*, 58 (1993) 4709.
55. R. Fornasier, F. Montanari, G. Podda, P. Tundo, *Tetrahedron Lett.*, 17 (1976) 1381.

56. K. -R. Kim, H. Kim, *J. Chromatogr. A*, 866 (2000) 87.
57. S. Motoyasu, M. Toshiyuki, *J. Pharm. Biomed. Anal*., 16 (1997) 139.
58. S. Rahavendran, H. Karnes, *Anal. Chem.*, 69 (1997) 3022.
59. S. L. Regen, *J. Am. Chem. Soc*., 97 (1975) 5956.
60. R. Annunziata, M. Benaglia, M. Cinquini, F. Cozzi, G. Tocco, *Org. Lett.*, 2 (2000) 1737.
61. E. J. Corey, F. Xu, M. C. Noe, *J. Am. Chem. Soc.*, 119 (1997) 12414.
62. P. Tundo, P. Venturello, *Inorg. Chim. Acta*, 40 (1980) 134.
63. T. Ido, T. Yamamoto, G. Jin, S. Goto, *Chem. Engin. Sci*., 52 (1997) 3511.
64. Y. Fiamegos, C. Konidari, C. Stalikas, *Anal. Chem.*, 75 (2003) 4034.
65. S. -H. Chen, H. -L. Wu, M. Tanaka, T. Shono, K. Funazo, *J. Chromatogr. A*, 502 (1990) 257.
66. S. Chen, S. Wu, H. Kou, H. Wu, *Anal. Toxicol.*, 18 (1994) 319.
67. H. Haber, H. M. Haber, M. F. Melzig, *Anal. Biochem*., 224 (1995) 256.
68. A. Miki, H. Tsuchihashi, H. Yamano, M. Yamashita, *Anal. Chim. Acta*, 356 (1997) 165.
69. Y. C. Fiamegos, C. G. Nanos, G. A. Pilidis, C. D. Stalikas, *J. Chromatogr. A*, 983 (2003) 215.
70. A. Arbin, H. Brink, J. Vessman, *J. Chromatogr. A*, 170 (1979) 25.
71. H. H. Maurer, J. W. Arlt, *J. Chromatogr. B*, 714 (1998) 181.
72. F. X. Zhou, I. S. Krull, B. Feibush, *J. Chromatogr.*, 648 (1993) 357.
73. A. Miki, H. Tsuchihashi, K. Ueda, M. Yamashita, *J. Chromatogr. A*, 718 (1995) 383.
74. A. Miki, H. Tsuchihashi, M. Yamashita, *J. Anal. Toxicol.*, 22 (1998) 237.
75. A. Miki, M. Katagi, H. Tsuchihashi, M. Yamashita, *J. Anal. Toxicol*., 23 (1999) 86.
76. A. Miki, M. Nishikawa, H. Tsuchihashi, *J. Health Sci*., 46 (2000) 81.
77. Y. C. Fiamegos, C. G. Nanos, J. Vervoort, C. D. Stalikas, *J. Chromatogr. A*, 1041 (2004) 11.
78. D. Mason, S. Magdassi, Y. Sasson, *J. Org. Chem.*, 55 (1990) 2714.
79. W. Lasek, M. Makosza, *J. Phys. Org. Chem*., 6 (1993) 412.
80. R. S. Juang, S. C. Liu, *Ind. Eng. Chem. Res*., 37 (1998) 4625.
81. M. L. Wang, In: *Kinetic modeling of catalytic phase transfer systems* (Y. Sasson, Newmann, R., (Eds.), Chapman & Hall: New York, (1997).
82. H. -S. Wu, T. -R. Fang, S. -S. Meng, K. -H. Hu, *J. Mol. Catal. A*, 136 (1998) 135.
83. S. Desikan, L. K. Doraiswamy, *Ind. Eng. Chem. Res.*, 34 (1995) 3524.
84. F. Montari, S. Quinci, P. Tundo, *J. Org. Chem*., 48 (1983) 199.
85. P. F. Marconi, W. T. Ford, *J. Catal.*, 83 (1983) 160.
86. M. L. Wang, H. M. Yang, *Ind. Eng. Chem. Res*., 30 (1991) 2384.
87. M. L. Wang, H. M. Yang, *Ind. Eng. Chem. Res*., 31 (1992) 1868.
88. S. D. Naik, L. K. Doraiswamy, Phase-Transfer Catalysis: Chemistry and Engineering. *A.I.Ch.E. J*., 44 (1998) 612.
89. E. Ruckenstein, L. Hong, *J. Catal.*, 136 (1992) 378.
90. N. Adinolfe, M. Bicking, *J. Chromatogr. Sci.*, 23 (1985) 407.