



ELSEVIER

Journal of Chromatography A, 969 (2002) 3–8

JOURNAL OF  
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Review

# Physicochemical measurements by the reversed-flow version of inverse gas chromatography

Nicholas A. Katsanos\*

*Physical Chemistry Laboratory, Department of Chemistry, University of Patras, P.O. Box 1045, 26504 Patras, Greece*

## Abstract

Since the first publication on the method, reversed-flow gas chromatography has been used to “separate” physicochemical quantities by measuring the value of one in the presence of another. The experimental arrangement consists of a small modification of a commercial gas chromatograph, so that it includes a four- or six-port gas sampling valve, and a simple cell placed inside the chromatographic oven. This cell suppresses the effects of the carrier gas flow on the physicochemical phenomena taking place in the stationary phase. These phenomena pertain to chemical kinetics, diffusion in gases, liquids and surfaces, mass transfer across gas–liquid and gas–solid boundaries, local adsorption on heterogeneous solid surfaces, etc.

© 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Reversed-flow gas chromatography; Diffusion; Propanol; Ethane; Calcium oxide

## Contents

1. Introduction .....	3
2. Theory and methodology .....	4
3. Potential of the methodology and discussion .....	6
4. Conclusions .....	7
Acknowledgements .....	7
References .....	7

## 1. Introduction

Reversed-flow gas chromatography (RF-GC) does not depend on retention times, broadening factors, and statistical moments of the elution bands, due mainly to non-linear isotherms, non-negligible axial

diffusion in the column, non-instantaneous equilibration between the mobile and the stationary phase, non-sharp input distribution of the analyte, etc. Also, the results of RF-GC do not need extrapolation to infinite dilution and zero carrier gas flow-rate to approximate true physicochemical parameters. This is because it is not an integration method, like those measuring concentrations as functions of time in chemical kinetics. It is a *differential method* measuring rates of physicochemical phenomena, not only

\*Corresponding author. Tel.: +30-61-997-110; fax: +30-61-997-144.

E-mail address: [rita@chemistry.upatras.gr](mailto:rita@chemistry.upatras.gr) (N.A. Katsanos).

initially, like initial rates of chemical reactions, but over an extended period of time, thus constituting a time-resolved chromatography.

The first idea on this differential aspect was that of Phillips et al. [1], who stopped the flow of the carrier gas for a short time period repeatedly, producing each time extra narrow peaks. By this procedure, he measured the differential rate of a catalytic reaction taking place on the stationary phase in a gas chromatographic column. The method permitted a direct determination of reaction rates, not only for small conversions to products, or for reaction times around zero, but in the whole range of conversions covering an extended period of time. Probably the main drawback of the method is that it continuously switches the system under study from a flow dynamic one to a static system and vice versa, by repeatedly closing and opening the carrier-gas flow. Diffusion and other related phenomena, which are usually negligible during the gas flow, may become important when the flow is stopped. It was to cure

this that the RF-GC version of inverse gas chromatography (IGC) was invented.

## 2. Theory and methodology

Initially [2–4], the reactant was injected at a middle point of the column containing a catalyst as the stationary phase, and the direction of carrier-gas flow was reversed from time to time instead of stopping it. This also created extra chromatographic peaks “sited” on the continuous signal. The next idea was to reverse the flow only for a short time period (5–60 s) and then restore it in its original direction. The result was a sharp symmetrical and narrow peak, its width at half-height being exactly equal to the duration of the flow reversal. An example is shown in Fig. 1.

A long series of such *sample peaks* can be obtained, but their use in calculating physicochemical quantities other than rate constants of heteroge-

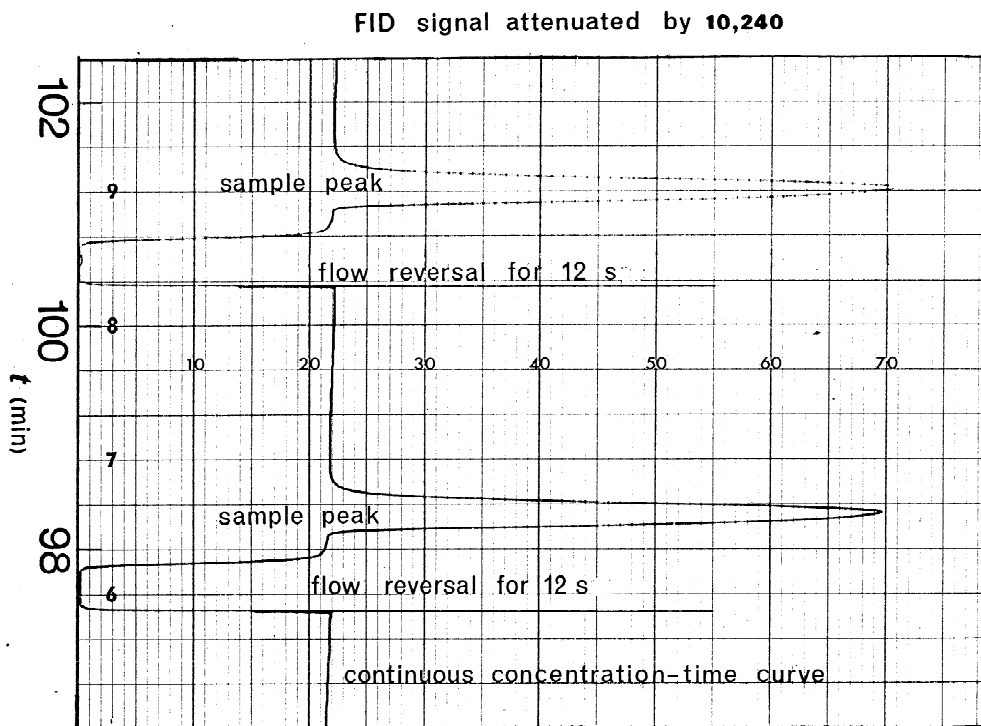


Fig. 1. A reversed-flow chromatogram of 1-propanol vapour diffusing into helium carrier gas ( $38.1 \text{ cm}^3/\text{min}$ ), at 342.4 K.

neous catalytic reactions became problematic, since a typical mass balance in the chromatographic column would be:

$$\frac{\partial c_g}{\partial t} = -v \cdot \frac{\partial c_g}{\partial x} + D_g \cdot \frac{\partial^2 c_g}{\partial x^2} + k_R(c_s - c_s^*) \quad (1)$$

where  $c_g$  is the concentration of analyte A in the gas phase (mol/cm<sup>3</sup>);  $t$  is the time (s);  $x$  is the length coordinate along the column (cm);  $v$  is the linear velocity of carrier gas (cm/s);  $D_g$  is the diffusion coefficient of A in the carrier gas (cm<sup>2</sup>/s);  $k_R$  is the rate constant for adsorption/desorption on the stationary phase (s<sup>-1</sup>);  $c_s$  is the concentration of A in the adsorbed state (mol/g);  $c_s^*$  is the equilibrium adsorbed concentration of A (mol/g).

The solution of such equations to find say  $k_R$  or  $c_s$  is very difficult, if not impossible, owing mainly to the presence of the term  $v(\partial c_g/\partial x)$ . Can we physically suppress the effects of this term on the last two terms on the right, describing physicochemical processes taking place in the gaseous and the stationary phase? The answer is yes, by simply placing the tube containing the stationary phase perpendicularly to the direction of the carrier gas flow. Thus, the term  $-v(\partial c_g/\partial x)$  is abolished from the GC equation, the carrier gas running only through the so-called “sampling column”, i.e. an empty gas chromatographic tube (100–160 cm × 4 mm I.D.) connected to the inlet of carrier gas at the one end and to the detector at the other, by means of a four-port gas sampling valve [5–9]. At about the middle of this column the tube containing the stationary phase was connected.

A small volume of the analyte gas is injected onto the solid bed through a common injector, closing the vertical tube. Two mass balance equations are written to describe its diffusion and adsorption on the solid of the vertical column, filled also with stagnant, not flowing, carrier gas. One is Eq. (1) without the term  $-v(\partial c_g/\partial x)$ , and the other simply reads:

$$\frac{\partial c_z}{\partial t} = D_z \cdot \frac{\partial^2 c_z}{\partial z^2} \quad (2)$$

where  $z$  denotes the length coordinate of the vertical part of the tube not containing any solid.

The rate of change of the adsorbed concentration  $c_s$  is:

$$\frac{\partial c_s}{\partial t} = k_R(c_s^* - c_s) - k_2 c_s \quad (3)$$

$k_2$  (s<sup>-1</sup>) being the rate constant of a possible first-order or pseudo-first-order surface reaction of the adsorbed A. An independent isotherm describes the local with respect to time equilibrium adsorbed concentration, without specifying a priori an isotherm model [10]:

$$c_s^* = \frac{m_s}{a_s} \delta(x - L_2) + \frac{a_x}{a_s} \cdot k_1 \int_0^t c_g(\tau) d\tau \quad (4)$$

where  $m_s$  is the amount of analyte A which would be adsorbed at equilibrium initially (mol/g);  $a_s$  is the amount of stationary phase per unit length of column bed (g/cm);  $L_2$  is the length of solid bed (cm);  $a_x$  is the cross sectional area of the void space in the solid bed (cm<sup>2</sup>);  $k_1$  is the local adsorption parameter, transforming the area under the  $c_g$  vs.  $t$  curve into  $c_s^*$  (s<sup>-1</sup>);  $\tau$  is a dummy variable for time.

The detailed solution of a similar system of partial differential equations can be found elsewhere [9]. This solution gives the value of  $c_z$  of Eq. (2) at the junction of the sampling and the vertical column ( $z = 0$ ), at time  $t$  when a flow reversal (for 5–60 s) of the carrier gas (flowing only through the sampling column) is made, by means of the four-port valve of the system. What is the form of this function  $c_z(0, t)$  and how is it measured experimentally? The form is a sum of 2–4 exponential functions of  $t$ , being proportional to the height  $H$  of the sample peaks (like those of Fig. 1) created and recorded by each flow reversal:

$$H^{1/M} = g c_z(0, t) = \sum_i A_i \exp(B_i t) \quad (5)$$

where  $M$  is the known response factor of the detector,  $g$  a calibration factor for each analyte calculated easily [10], and  $A_i, B_i$ , are functions of the physicochemical quantities pertaining to the various phenomena taking place in the stationary phase bed.

The above answers the question, “why a carrier gas is flowing in the system”, remembering that it does not flow through the stationary phase. The answer is “to carry out a sampling procedure of the gaseous phase, coming out of the stationary phase bed because of a diffusion current”. The sampling

position is the junction at  $z = 0$ . A long asymmetrical chromatographic band would be obtained, unless the four-port valve is turned to the other position and then returned to its original position after 5–60 s. This causes a short flow-reversal of the carrier gas in the sampling column, creating in the recording system sharp symmetrical and narrow peaks. An auxiliary separation column is used in front of the detector when two or more products come out at the junction  $z = 0$ .

Thus, we are left with a long series of narrow sample peaks, their height  $H$  from the continuous signal being given by Eq. (5).

The summation index  $i$  may range from 1 to 2, 3 or 4, depending on the mathematical model employed for the description of the various physicochemical processes, and the approximations used to solve the relevant system of partial differential equations. In all cases,  $A_i$  and  $B_i$  are calculated by personal computer programmes written for non-linear least-squares regression analysis. The form of Eq. (5) is not an a priori assumption, but results from the mathematical solutions.

### 3. Potential of the methodology and discussion

To mention only some of the quantities measured, one can determine the following from  $A_i$  and  $B_i$ .

- (1) Chemical kinetics parameters in heterogeneous and homogeneous catalysis [3,11–18,20,21].
- (2) Diffusion coefficients in gases and liquids [22–26].
- (3) Rates of evaporation of pure liquids [27].
- (4) Activity coefficients in liquid mixtures [28,29].
- (5) Mass transfer and partition coefficients across gas–liquid and gas–solid boundaries [30–37].
- (6) Obstructive factors and external porosities in solid beds [38].
- (7) Rate constants in bimolecular gaseous reactions [39,40].
- (8) Overall and differential experimental isotherms of adsorption [10,41–43].

The list of references given above is by no means exhaustive. Only representative publications are cited.

In some of the above applications (1–5) the vertical column contains a liquid instead of a solid.

In (7) it contains only the reacting gases, and in (8) it is a diffusion denuder tube having its internal wall covered with a thin layer of solid particles.

Some recent achievements of physicochemical measurements by RF-GC are the following.

- (9) The local adsorption rate constant, the desorption rate constant, the surface reaction rate constant, the deposition velocity, the reaction probability, and the apparent gaseous reaction rate constant were measured, together with a simultaneous determination of the isotherm, for the adsorption of gases on solid surfaces [19].
- (10) The local adsorption energies  $\varepsilon$ , the local monolayer capacities  $c_{\max}^*$ , the local adsorption isotherms  $\theta_i$ , and the adsorption energy distribution functions  $f(\varepsilon)$ , for adsorption of gases on heterogeneous surfaces were measured in time-resolved surface heterogeneity studies, circumventing altogether the well-known integral equation [44–48]:

$$\Theta(p, T) = \int_0^{\infty} \theta_i(p, T, \varepsilon) f(\varepsilon) d\varepsilon \quad (6)$$

where  $\Theta(p, T)$  is the overall experimental adsorption isotherm.

- (11) The time separation of three kinds of adsorption sites of gases on heterogeneous surfaces was experimentally found [49].
- (12) The energy of lateral molecular interactions on heterogeneous surfaces was measured in a time-resolved procedure [50].

Tables of results showing the adsorption properties of various adsorbates on heterogeneous solids can easily be obtained (cf. Table 1 in Ref. [44]) showing that the reversed-flow version of IGC constitutes a time-resolved surface heterogeneity study. All quantities change regularly with the time of sampling the surface, although the changes are neither linear nor chaotic. The various quantities can be graphically plotted, not only against time but also as functions of each other. For example, in Fig. 2 the new adsorption energy distribution function  $\varphi(\varepsilon; t) = \theta_t f(\varepsilon) / c_{\max}^*$  for the system ethane/calcium oxide, at 50 °C is plotted against the random variate of adsorption energy  $\varepsilon$  in (a), and against the structural parameter of time  $t$  in (b). In (c), the time profile of the lateral

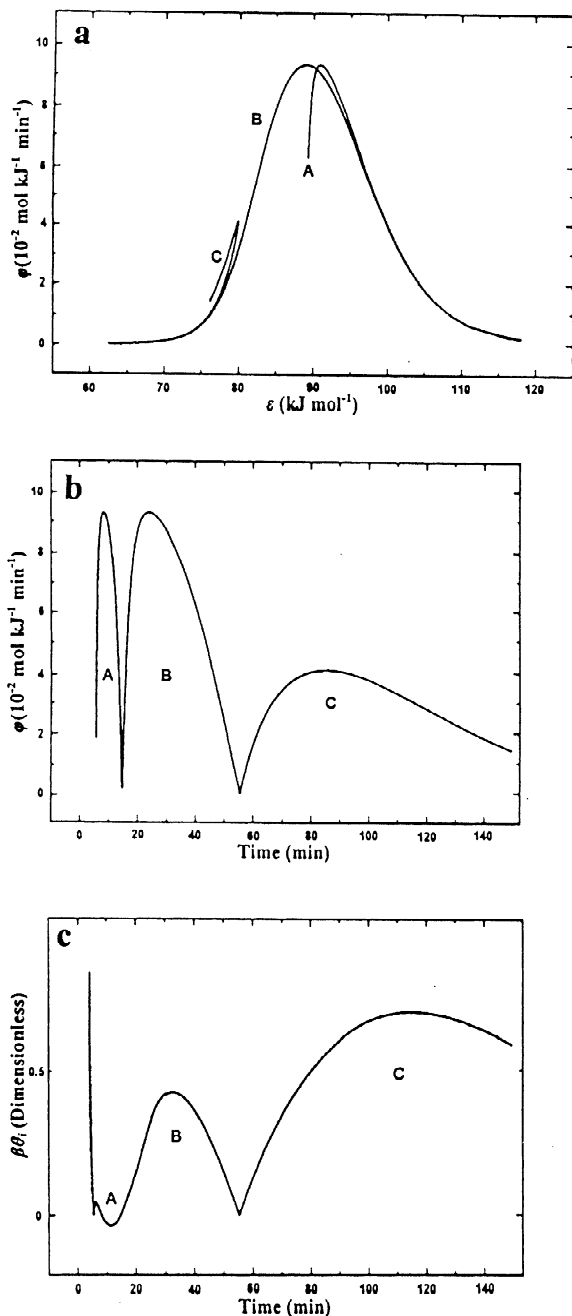


Fig. 2. For the system ethane/calcium oxide, at 323.2 K, the energy distribution function  $\phi(\epsilon; t) = \theta_i f(\epsilon) / c_{\text{max}}^*$  is plotted: (a) against the random variate  $\epsilon$ ; (b) against the structural parameter of time  $t$ ; (c) for the same system, the lateral molecular interaction energy  $\beta\theta$ , is plotted against the experimental time  $t$ .

interaction energy  $\beta\theta$ , is shown. The plot (a) has the appearance of three superimposed Gaussian curves A, B and C; the plot in (b) shows an almost perfect way to separate the three Gaussian-shaped probability distributions A, B and C; finally, the plot in (c) is in accord with the model of three kinds of adsorption sites, as proposed by Bakaev and Steele [51].

#### 4. Conclusions

From the previous section and the literature cited it is obvious that, using a conventional simple chromatograph slightly modified to include a four- or six-port gas sampling valve, one can easily and accurately measure physicochemical quantities never having been measured before, e.g. lateral molecular interactions of molecules on heterogeneous surfaces [50].

More work is well under way concerning the application of the RF-GC version for the determination of the surface diffusion coefficients and the effectiveness factors on the heterogeneous surfaces of solid catalysts, the surface energy of solids, and adsorption kinetics on heterogeneous surfaces.

#### Acknowledgements

The author expresses his gratitude to the International Advisory Committee of the 1st International Conference on Inverse Gas Chromatography, for the kind invitation to present the work outlined here as an invited lecture. He is also obliged to Miss Anna Malliori for her kind assistance in the preparation of the work.

#### References

- [1] C.S.G. Phillips, A.J. Hart-Davis, R.G.L. Saul, J. Wormald, J. Gas Chromatogr. 5 (1967) 424.
- [2] N.A. Katsanos, I. Georgiadou, J. Chem. Soc. Chem. Commun. (1980) 242.
- [3] N.A. Katsanos, J. Chem. Soc. Faraday Trans. 178 (1982) 1051.
- [4] N.A. Katsanos, G. Karaiskakis, Adv. Chromatogr. 24 (1984) 125.

- [5] N.A. Katsanos, in: *Flow Perturbation Gas Chromatography*, Marcel Dekker, New York, 1988, p. 87.
- [6] N.A. Katsanos, in: F. Dondi, G. Guiochon (Eds.), *Theoretical Advancement in Chromatography and Related Separation Techniques*, Kluwer, Amsterdam, 1992, p. 349.
- [7] N.A. Katsanos, F. Roubani-Kalantzopoulou, *J. Chromatogr. A* 710 (1995) 191.
- [8] N.A. Katsanos, R. Thede, F. Roubani-Kalantzopoulou, *J. Chromatogr. A* 795 (1998) 133.
- [9] N.A. Katsanos, F. Roubani-Kalantzopoulou, *Adv. Chromatogr.* 40 (2000) 231.
- [10] V. Sotiropoulou, G. Vassilev, N.A. Katsanos, H. Metaxa, F. Roubani-Kalantzopoulou, *J. Chem. Soc. Faraday Trans.* 91 (1995) 485.
- [11] M. Kotinopoulos, G. Karaiskakis, N.A. Katsanos, *J. Chem. Soc. Faraday Trans.* 1 78 (1982) 3379.
- [12] G. Karaiskakis, N.A. Katsanos, A. Lycourghiotis, *Can. J. Chem.* 61 (1983) 1853.
- [13] N.A. Katsanos, G. Karaiskakis, A. Niotis, *J. Catal.* 94 (1985) 376.
- [14] N.A. Katsanos, G. Karaiskakis, *J. Chromatogr.* 395 (1987) 423.
- [15] V. Ioffe, N.A. Katsanos, L.A. Kokovina, A.N. Marinitsev, B.V. Stolyarov, *Kinet. Kataliz* 28 (1987) 805.
- [16] N.A. Katsanos, *Catal. Today* 2 (1988) 605.
- [17] B.V. Stolyarov, N.A. Katsanos, P. Agathonos, J. Kapos, *J. Chromatogr.* 550 (1991) 181.
- [18] I. Topalova, A. Niotis, N.A. Katsanos, V. Sotiropoulou, *Chromatographia* 41 (1995) 227.
- [19] Ch. Abatzoglou, E. Iliopoulou, N.A. Katsanos, F. Roubani-Kalantzopoulou, A. Kalantzopoulos, *J. Chromatogr. A* 775 (1997) 211.
- [20] N.A. Katsanos, F. De Santis, A. Cordoba, S. Massa, F. Roubani-Kalantzopoulou, *J. Hazard. Mater.* 64 (1999) 21.
- [21] D. Gavril, N.A. Katsanos, G. Karaiskakis, *J. Chromatogr. A* 852 (1999) 1507.
- [22] N.A. Katsanos, G. Karaiskakis, *J. Chromatogr.* 237 (1982) 1.
- [23] N.A. Katsanos, G. Karaiskakis, *J. Chromatogr.* 254 (1983) 15.
- [24] G. Karaiskakis, N.A. Katsanos, A. Niotis, *Chromatographia* 17 (1983) 310.
- [25] N.A. Katsanos, J. Kapos, *Anal. Chem.* 61 (1989) 2231.
- [26] S.S. Nikolopoulos, E. Arvanitopoulou, N.A. Katsanos, *Fresenius J. Anal. Chem.* 352 (1995) 639.
- [27] G. Karaiskakis, N.A. Katsanos, *J. Phys. Chem.* 88 (1984) 3674.
- [28] N.A. Katsanos, G. Karaiskakis, P. Agathonos, *J. Chromatogr.* 349 (1986) 369.
- [29] M. Roth, A. Koliadima, G. Karaiskakis, N.A. Katsanos, *J. Chromatogr.* 595 (1992) 237.
- [30] E. Dalas, G. Karaiskakis, N.A. Katsanos, A. Gounaris, *J. Chromatogr.* 348 (1985) 339.
- [31] G. Karaiskakis, P. Agathonos, A. Niotis, N.A. Katsanos, *J. Chromatogr.* 364 (1986) 79.
- [32] N.A. Katsanos, E. Dalas, *J. Phys. Chem.* 91 (1987) 3103.
- [33] N.A. Katsanos, P. Agathonos, A. Niotis, *J. Phys. Chem.* 92 (1988) 1645.
- [34] N.A. Katsanos, Ch. Vassilakos, *J. Chromatogr.* 557 (1991) 469.
- [35] Ch. Vassilakos, N.A. Katsanos, A. Niotis, *Atmos. Environ.* 26A (1992) 219.
- [36] I. Topalova, N.A. Katsanos, J. Kapos, Ch. Vassilakos, *Atmos. Environ.* 28 (1994) 1791.
- [37] S. Nikolakaki, Ch. Vassilakos, N.A. Katsanos, *Chromatographia* 38 (1994) 191.
- [38] N.A. Katsanos, Ch. Vassilakos, *J. Chromatogr.* 471 (1989) 123.
- [39] V. Sotiropoulou, N.A. Katsanos, H. Metaxa, F. Roubani-Kalantzopoulou, *Chromatographia* 42 (1996) 441.
- [40] F. Roubani-Kalantzopoulou, E. Kalogirou, A. Kalantzopoulos, H. Metaxa, R. Thede, *Chromatographia* 46 (1997) 161.
- [41] E. Arvanitopoulou, N.A. Katsanos, H. Metaxa, F. Roubani-Kalantzopoulou, *Atmos. Environ.* 28 (1994) 2407.
- [42] N.A. Katsanos, F. Roubani-Kalantzopoulou, *J. Chromatogr. A* 710 (1995) 191.
- [43] G. Vassilev, N.A. Katsanos, *Ann. Univ. Sofia Fac. Chim.* 89 (1997) 27.
- [44] N.A. Katsanos, E. Arvanitopoulou, F. Roubani-Kalantzopoulou, *J. Phys. Chem. B* 103 (1999) 1152.
- [45] N.A. Katsanos, N. Rakintzis, F. Roubani-Kalantzopoulou, E. Arvanitopoulou, A. Kalantzopoulos, *J. Chromatogr. A* 845 (1999) 103.
- [46] N.A. Katsanos, E. Iliopoulou, F. Roubani-Kalantzopoulou, E. Kalogirou, *J. Phys. Chem. B* 103 (1999) 10228.
- [47] Ch. Abatzoglou, N.A. Katsanos, A. Kalantzopoulos, F. Roubani-Kalantzopoulou, *Stud. Surf. Sci. Catal.* 122 (1999) 175.
- [48] N.A. Katsanos, E. Iliopoulou, V. Plagianakos, H. Mangou, *J. Colloid. Interf. Sci.* 239 (2001) 10.
- [49] F. Roubani-Kalantzopoulou, Th. Artemiadi, I. Bassiotis, N.A. Katsanos, V. Plagianakos, *Chromatographia* 53 (2001) 315.
- [50] N.A. Katsanos, F. Roubani-Kalantzopoulou, E. Iliopoulou, I. Bassiotis, V. Siokos, M.N. Vrahatis, V.P. Plagianakos, *Colloid Surf. A* 201 (2002) 173.
- [51] V.A. Bakaev, W.A. Steele, *Langmuir* 8 (1992) 1372.