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# Diffusion as a Basis for the Determination of Physicochemical Quantities by RF-IGC

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## 1. Introduction

Progress in many areas of the material science and engineering requires the development of new advanced methods for studying processes taking place at boundaries between phases. That is the case of the method of Reversed Flow – (Inverse) Gas Chromatography (RF-GC or RF-IGC), which represents a tool for studying gas-solid interfaces. In contrast to classical chromatography the RF-IGC method is interested in the stationary phase properties rather than in those of the solutes. Thus, this method provides information about the behavior of materials surfaces in different environments [1-4].

## 2. How the RF-IGC leads to physicochemical quantities through the diffusion

The RF-IGC method [2,5] involves a flow-rate perturbation of the carrier gas which is achieved experimentally by using a four port gas sampling valve and reversing the direction of flow of the carrier gas, usually for a short time interval. If pure carrier gas passes through the sampling column, nothing happens on reversing the flow. If a solute comes out of the diffusion column (cf Fig. 1) as the result of its diffusion into the carrier gas, the flow reversal records the concentration of the solute at the junction of the sampling column with that of the diffusion one, at the moment of the reversal. This concentration recording has the form of extra chromatographic peaks superimposed on the otherwise continuous detector signal (cf Fig. 2).

The theoretical analysis for the measurement of the desired physicochemical parameters by RF-GC depends on the phenomena being studied and the accuracy adopted. By plotting ln$H$ against $t$, one obtains the so-called diffusion bands [2]. All physicochemical quantities are calculated from the diffusion bands, by deriving an equation which describes them mathematically. This was based on the solution of a system of four partial differential equations, under given initial and boundary conditions. The main equation, describing the diffusion bands, is:

$$H^{1\backslash M} = A_1 \exp(B_1 t) + A_2 \exp(B_2 t) + A_3 \exp(B_3 t) \quad (1)$$

where $M$ is the response factor of the detector, $g$ is a calibration factor, and $c(l',t)$ the concentration of the reactant at $x = l'$ and time $t$.

By entering the values of the pairs $H$ (peak height), $t$ (time of reversal) in a suitable PC programme[5] the exponential coefficients and the pre-exponential factors of Eq. (1) are computed by a non-linear least-squares fitting. From these it is possible to determine several physicochemical quantities, namely: (1) local adsorption energy, (2) local monolayer capacity, (3) local adsorption isotherm, (4) density probability function, (5) non-adsorbed gas concentration above the oxide at equilibrium, (6) energy from lateral interactions. Moreover, three kinetic parameters are also determined, $k_1$(adsorption ), $k_{-1}$ (desorption ) and $k_2$ ( surface heterogeneous reaction). The above calculated quantities refer to the adsorption of two gases, that is $C_2H_6$ and $C_2H_4$ on five oxides ($Fe_2O_3$, $TiO_2$, PbO, ZnO, $Cr_2O_3$).

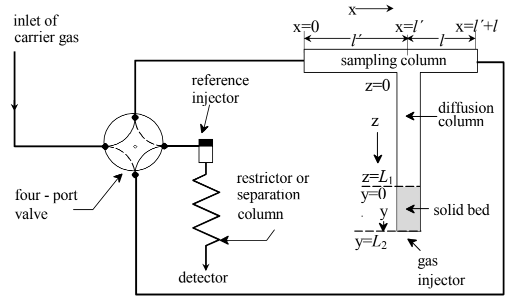

Fig. 1: Schematic representation of the RF-IGC set-up for the study of physicochemical quantities for surface characterization through the diffusion of gases

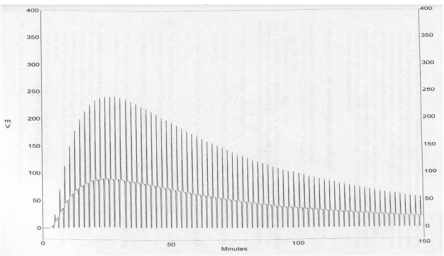

Fig. 2: Diffusion of ethylene in nitrogen, in the presence of $TiO_2$

## 3. Conclusion

The adsorption of two gases, that is $C_2H_6$ and $C_2H_4$, is investigated. The adsorbents used were five oxides, namely $Fe_2O_3$, $TiO_2$, PbO, ZnO, $Cr_2O_3$. Thus, a systematic study of ten heterogeneous systems and their characterization through some local physicochemical parameters is achieved. The method used is the RF-IGC, a well known version of inverse gas chromatography, which has the stationary phase of the heterogeneous system as its object of investigation.

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