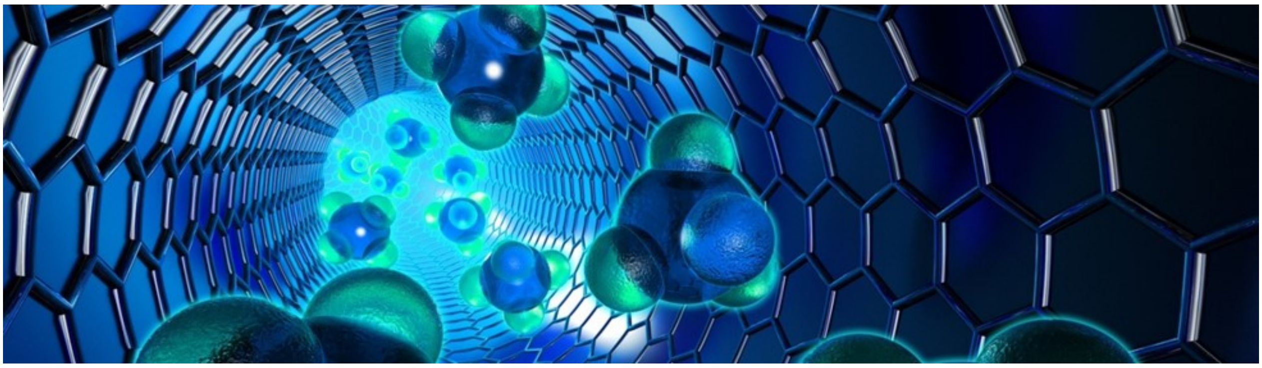

Case studies of using inverse gas chromatography in pharmaceutics

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The method of inverse gas chromatography (iGC) is becoming increasingly popular in pharmaceutical technology. A growing number of users profile the surface energies of drug substances and/or of galenical products. This talk provides a brief overview of different applications in pharmaceutical technology that are followed by selected industrial case studies in which iGC was playing a major analytical role. A particular focus is made on measuring lot-to-lot variability with respect to further processing of drug substance. It is discussed that modern equipment of iGC appears to have high potential in research as well as pharmaceutical development and manufacturing.

Is the concentration gradient approach useful for inverse chromatography?

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Gradient concentration was pioneering by Tiselius [1] in 1952, later the temperature gradient turns out to be indispensable for the gas chromatographic analysis of products having a very different volatility. Some years later, precision volumetric micro-pumps permit to realize concentration gradient for performing separation of molecule exhibiting very different polarity by analytical liquid chromatography.

But, to our knowledge, no inverse chromatographic experiments were published which were calling on the use of a gradient. In 1996, Eric Brendlé had led a study of adsorption of antifouling additives, which had demonstrated the high potential of this approach. Comparatively with frontal analysis, it permits to have access very easily to both adsorption and desorption isotherms and moreover, by changing the slope of the gradient, to evidence kinetic phenomena. Unfortunately, no further experiments were led on this topic

Does gradient approach could be extended to inverse gas chromatography at finite concentration? The answer is “Yes”, when using a very simple device derived from the Tiselius’s one. Simulations, done on computer, will demonstrate the potentialities of such approach, which will certainly improve the precision of the acquisition of both adsorption and desorption isotherm in a larger domain of relative partial pressure.

[1] R.J.P.Williams, A.Tiselius, Gradient elution analysis. 1-A general treatment, Acta Chemica (1952)

Determination of AL_2O_3 Surface Concentration on Rutile TiO_2 Particles

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IGC (Inverse Gas Chromatography) was developed during the last 20 years and is used as method in the field of particle technology and for carbon-, Al_2O_3– and SiO_2–particle surface analysis.

The content of the method is to measure surface properties of particles via the adsorption behavior of disperse and acid or base probe molecules interacting with the particle surface. In general there are two regimes of concentration of probe molecules which are offered to the sample surfaces, where measurements can be done. Infinite dilution of the probe molecules as well as finite concentration of the probe molecules can be used delivering different information about the sample-probe interaction.

Within the presented study of TiO_2-particles, doped with different amounts of Al_2O_3, strengths and weaknesses of IGC can be identified.

With rising Al_2O_3-concentration the disperse Free Surface Energy Υ_s^D as well as the Acid Base Surface Energy Υ_s^{AB} decreases. For both energies this decrease shows a resolution of the method better than 0,01 % of mass, with respect to the mass of TiO_2.

Inverse chromatography technics for surface properties characterization of materials used in aeronautical and space applications

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Interactions between the components of complex composite materials systems are crucial for their implementation. The usefulness of Inverse Chromatography technics (IGC and ILC) and surface chemical analysis technics (TOF SIMS) is demonstrated in two different applications :

1. Silicon Carbide powder (SiC), used in Ceramic Matrix Composite for high temperature gas turbine engine components

Relations between surface chemical structures and the kind and strength of surface interactions are set up on about ten SiC powders.

2. Rubber plate, used in propellant assembly, as thermal insulation of the booster metallic structure.

In this application, a good adhesion between the different components of the assemblage is crucial and requires knowledge of the interaction mechanism between these components and the thermal insulation.

The Inverse Liquide Chromatography technic (ILC) s is appropriate to determine kind and strength of the chemical interactions between mobile constituents and the rubber.

Determination of Hansen Solubility Parameters for Solid Materials by Means of Inverse Gas Chromatography

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Inverse gas chromatography might be successfully used for the determination of Hansen Solubility parameters (HSPs). Values of dispersive, polar and hydrogen bonding components of solubility parameter are used in the prediction of the behaviour of, e.g. the pharmaceutically active material in real mixture, e.g. interactions with excipients. Values of HSPs parameters are close to that obtained from additive method of Hoftyzer/van Krevelen procedure. However, these seconds can be calculated if the structure of examined material is known. It is impossible for mixtures or species having unknown structure. In such a case, the use of inverse gas chromatography is suggested.

Characterization of tailored porous carbons by Inverse Gas Chromatography

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Inverse gas chromatography (IGC) is a fast and versatile technique to determine thermodynamic properties of solids. Thermodynamic properties (e.g. dispersive surface energy, surface polarity and acid-base properties) are obtained on the basis of several chromatograms of different non-polar and polar gaseous probe molecules. These thermodynamic properties are significant for a better understanding and further development of porous materials. In this study, IGC was intended to analyze the surface chemistry in relation to the sorption behavior of activated carbon sorbents derived from novel resorcinol-urea-formaldehyde (RUF) resin. The dispersive surface energy, nanoroughness, surface polarity and acid-base properties were determined and the correlations between surface chemistry and final sorption performance were systematically analyzed. Further sorption property optimization of the carbon materials was conducted based on the IGC and the best candidate materials with optimized properties were benchmarked against commercially available activated carbons and silica gel for the application in adsorption heat pumps.

Inverse Liquid Chromatography in surface characteristic of ceramic biomaterials

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Examination of the properties of the biomaterial surface layer is essential when adsorptive or adhesive properties should be estimated. Determination of the parameters, informing about the ability of the surface to different types of intermolecular interactions can be useful in analyzing, e.g. the influence of the surface modification on its characteristic or the behavior of cells in cultures in the living organism.

Application of inverse liquid chromatography seems to be useful to direct study of solid – liquid interaction in real conditions, which include: proper concentration, pressure, temperature and pH. This technique, with conjunction with proper models, allows to evaluate the physicochemical characteristic of the biomaterials surface e.g. its capacity to donor-acceptor interactions. In ILC, by changing the composition of the mobile phase in biomaterials surface characteristic, we are able to recreate conditions similar to those present in a living organism. In such a case the behavior of surface functional groups may be similar to that in real system.

It should be noted that test solute behavior in the ILC system is more complicated than in IGC. Although the difference between the IGC and the ILC refers only to the use of liquid instead of gas as the mobile phase, mechanisms of chromatographic processes is significantly different from each other. In ILC all measurements are the result of effective competition between solute and a mobile phase, which interact with the column filing. In IGC the mobile phase, the inert gas is virtually inactive and solute can be directly subjected to the adsorption process. The ILC the competitive adsorption/desorption processes of the test compound or the mobile phase may occur. In addition, mobile phase composition may affect the sorption properties of the stationary phase and thus their ability to interact with the test compound.

Explanation and understanding of these factors can significantly seem to be essential for a correct assessment of the properties of the surface layer of ILC technique.

Adsorption Enthalpies of Organic Molecules To Graphene, Graphite and Fluorographite

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Quantification and understanding of the interaction of adsorbed molecules to graphene represents a challenging topic in non-covalent functionalization of graphene.[1, 2] We measured adsorption enthalpies of volatile organic molecules[3] to flaky carbon-based nanomaterials (graphene, graphite and fluorographite) by inverse gas chromatography. For acetone we fitted the adsorption enthalpies and estimated the number of high-energy sites on graphene and graphite. Using theoretical calculations we showed that the high-energy sites are likely localized on surface steps and edge-cavities.[4] We also rationalized the complex behavior of adsorption enthalpies of ethanol on both materials and concluded that the ethanol molecules cluster on the hydrophobic surface.[5] The isosteric adsorption enthalpies of the volatile organic molecules to graphite and fluorographite are very similar. We calculated the adsorption enthalpies by various theoretical methods using two graphene models: coronene and infinite graphene.[6] The calculations indicated that the interactions of organic molecules to graphene are governed by London dispersive forces (amounting to 60% of attractive interactions), even for the polar molecules. The results showed that the adsorption enthalpies were largely controlled by the interaction energy.[3]

[1] Georgakilas et al. Chem. Rev., 112, 6156, 2012.
[2] Lazar et al. ACS Nano, 7, 1646, 2013.

[3] Lazar et al. J. Am. Chem. Soc., 135, 6372, 2013.
[4] Lazar et al. Carbon, 73, 448, 2014.
[5] Karlický et al. J. Phys. Chem. C, 119, 20535, 2015.
[6] Pykal et al. Phys. Chem. Chem. Phys., 18, 6351, 2016.