Numerical Simulation of Photoacoustic Measurements and Development of Measurement Postprocessing Methods

PhD Thesis

Author: Tibor Guba

Doctoral School of Physics

Department of Optics and Quantum Electronics

University of Szeged, Faculty of Science and Informatics

Supervisor:

Prof. Dr. Zoltán Bozóki

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I. Introduction

Diffusion is a mass transport phenomenon driven by the concentration gradient of mixtures of materials. Its name originates from the Latin expression diffundare which means spread out.

Diffusion is present in many natural processes. E.g. placing a bulk solid in a liquid the solid object gradually dissolves over time with a homogenous concentration throughout the volume of the liquid. The soil contains many solid and liquid components (e.g. water and oil). The dynamics of these components are governed by not just the pressure conditions, but also diffusional processes. Cellular metabolism is made possible by the permeative exchange of nutrients through the cells membrane. Pollutants do usually do not only spread through convective means, their transport has a significant diffusive component. The combination of diffusion and convection is called advection.

Countless industrial applications are known of the theory of diffusion processes. Examples of harmful diffusion:

- When transporting gases (like natural gas) through flexible rubber or polymer pipes the issue of gas loss may arise if the chosen material of the pipe is highly permeative.
- The same issue applies to rubber hoses used in tires.

- Many protective gear (e.g. rubber gloves and gas mask) rely on weak diffusive properties to insulate their users from harmful chemicals.
- Nuclear waste may also spread through diffusion. When designing containers for radiative waste one must take into account the prevention of this type of leaking.

Examples of useful diffusion:
- Food packaging defends the product from pollutants and conserves the goods. However, certain food need breathing packaging that lets through optimal amount of air for preserving the moisture and the texture.
- The precise doping of semiconductors is done by diffusive technologies.
- Carburization (diffusion of carbon) can significantly improve metals.
- Pervaporation.

The main focus of my thesis is the diffusion of gases though polymer and rubber membranes. The collaboration of the Department of Optics and Quantum Electronics, the Photoacoustics Reasearch Group and Contitech Rubber Industrial Ltd. has proven that the photoacoustic gas detection has many advantages in assessing gas permeation parameters.

II. Scientific Goals

The importance of permeation measurements increased with the widespread application of polymers and rubbers. In many cases the most important property regarding the applicability of a polymer is its permeability. Certain applications require the minimization of the gas permeative parameters. E.g. protective gears, flexible pipes. Other cases require the gas permeation parameters to be optimized (e.g. breathing food packaging). It is also possible to design gas-specific polymers that let through certain gases while insulating others. The specific diffusion makes separation techniques possible like pervaporation.

These applications make it clear that many requirements apply to permeation measurements. Unfortunately many widespread measurement methods and devices do not meet these requirements or meet them insufficiently. One of the basic requirements is a high reliability during a long stable and unattended/automated operation. A frequent complaint about the currently available technologies is that the accuracy and the repeatability of the measurements cannot achieve lesser values than 10%. Another common complaint is that the operation of these instruments requires extensive training and highly skilled personnel. Depending on the sample the problem of long measurement times also arise (days sometimes weeks). Often the selectivity of the instruments is not guaranteed. The measurements usually have a high cost and are labor intensive. Certain

industries (like the oil-industry) require the measurements to be conducted at high pressures, which is a challenging task

Taking into account all the above I conducted my research with the aim of quantitatively assessing the reliability of the measurement configuration used by the Photoacoustic Research Group at various conditions. My objective was also to develop mathematical and experimental methods to eliminate the distorting effects of the measurement system.

I worked on the following subtasks to achieve these goals:

1.   The quantitative assessment of the apparent gas permeation parameters' dependence of the carrier flow rate. Knowing the relationship of these quantities makes extrapolation of the results obtained at low carrier flow rates (and improved signal-to-noise ratio) possible.

2.   Analysis of the effects of various common measurement errors (offset error, time shift, high noise level, insufficient measurement time) on the of the gas permeation parameters' accuracy. I carried out this task by applying simulated errors on both real and simulated permeation curves. Through this analysis the confidence regions of the gas permeation parameters become quantifiable. The analysis also reveals the minimal experimental conditions required for reliable

measurements. As part of the subtask I compared the performance of the time-lag method and the full curve fitting method.

3. The elimination of the distorting effects of the measurement system through the application of systems theoretical and reactor technical methods. The goal of this subtask was to calculate the undistorted permeation curves for more precise post processing of the experiments.

III. Applied Methods

III.1. The analysis of the permeation curve's carrier rate dependence

We conducted permeation measurements for 4 different samples at varying v carrier rates. It was well known in advance that to achieve a sufficiently reliable result, the measurement must be conducted at high carrier rates. However, high carrier rates significantly increase the detected noise level, and for certain samples sufficiently high carrier rates are not even achievable. The applied experimental setup can be seen in Fig. 1.

The carrier gas was N_2 with 99,9995% purity. Two analytes were implemented during the experiments: CH_4 (99,995%) and CO_2 (99,9995%).
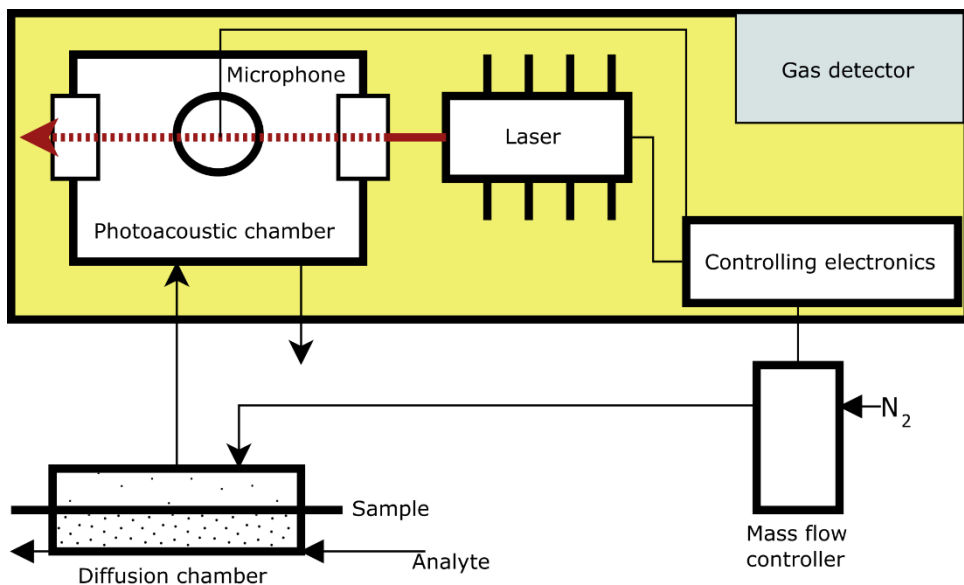
Figure 1. Carrier flow measurements experimental setup.

III.2. Analysis of the effects of distortions of the permeation curves

To visualize and quantify the propagation of the measurement errors to the gas permeation parameters I applied 4 different transformations with varying values on permeation curves (both measured and simulated). These transformations were: for offset errors vertical shift, for time shift horizontal shift, for increased noise the appliance of normally distributed random constants, for insufficient measurement times the truncation of the data. The resulting permeation curves yielded new – distorted – apparent permeation parameters, whose relationship to the magnitude of the transformations was evaluated.

III.3. Systems theoretical investigation

For the elimination of the measurement system's distorting effects the best performing system representation proved to be the Residence Time Distribution analysis known from the mathematics of the chemical reactor design. Similarly to the former subtask measured and simulated permeation curves were implanted in these calculations too. However, the curves were used in their numerically fitted forms because of the severe noise sensitivity of the deconvolution operation. The C permeation curves measured at $v = \infty$ carrier rate were considered to be undistorted. Therefore, the E Residence Time Distributions were calculated the following way:

$$E(t,v) = C(t,v) \frac{1}{*} C(t,\infty) \tag{1}$$

IV. Summary

During my PhD studies I absolved several important concepts of the diffusion theory and I gained deep knowledge of the Time-Lag and Carrier Flow measurement methods. Through my research I acquired extensive knowledge of programming and automation of postprocessing calculation, and adapted learnt several methods for system analysis.

My work revealed the unique measurement issues of the Time-Lag and Carrier Flow experimental setups. Our research yielded a relationship between the fitted gas permeation parameters and the carrier flow rates of the measurements that returned the data to be fitted. Through comparison studies I managed to prove that the Carrier Flow arrangement outperforms the Time-Lag arrangement in all but one cases (that one being the case of extremely fast permeation processes). My research also provided a novel mathematical procedure that improves the inherently distorted permeation curve measurement data.

Abstract of the PhD dissertation. Phrasing the new results,

§1. The experts of the Photoacoustics Research Group proved that the (widely applied) Time-Lag Measurement Method's output (measured gas permeation parameters) depends on the carrier flow rate used in the experimental setup.

In the published study about this experimental issue 4 different membrane samples were used. To quantify the results' dependence of the carrier flow rate the permeation curves of the used samples were analysed at several v[sccm] carrier rates on room temperature.

Through postprocessing calculation I managed to fit an exponential like dependence of the carrier flow rate for the diffusivity, permeability and

solubility of the samples. However, the results were not independent of the sample materials.

During my research I successfully unified the resulting $D(v), S(v), P(v)$ curves using the Carrying Efficiency as a scaling factor. The Carrying Efficiency also proved to be dependent of the sample material (precisely its Time-Lag). [66]

§2. The new results regarding the carrier rate dependence of the assessed parameters suggested a new direction for the research. In the upcoming project the team switched from the Time-Lag experimental setup to the very similar Carrier Flow measurement. This change addressed several gas technical issues of the former setup (leakage, monitoring of pressure on the detectors side of the diffusion). However the new setup required the development of new postprocessing software too. In my research I implemented an optimized Look-Up Table solution for the fitting of the permeation curves specific to the Carrier Flow arrangement**Error! Reference source not found.**. I deducted connections between the fitting parameters and the inflexion point and the plateau of the permeation curves that made the automatization of estimating the starting values of the fit possible. With the information detailed in **§1.** and the usage of simulated permeation curves I analyzed the four transformations' effects on the fitting parameters (for both the Time-Lag and Carrier Flow setups): truncation, time shift, offset error and noise increase. The results showed that valuable time can be saved by conducting the measurements only to a certain time-

limit. The verdict of the study was that the Carrier Flow Method proved to be more reliable in every scenario except the time shift.

§3. There are certain cases during measurement where sufficient carrier flow rates are not achievable (e.g. excessive noise level, high permeability samples). In these cases the permeation curves get distorted resulting in incorrect gas permeation parameters outputs. The aim of my later research processes was to eliminate the aforementioned distortions at low carrier flow rates. For the calculations I used the a priori knowledge from the former studies that suggested that the effect of the measurement system diminishes with increasing carrier rates. To obtain the Residence Time Distributions of the system for various carrier rates I deconvolved the sufficiently fast results from the slow ones (both in real and simulated cases). It is easily provable that the Residence Time Distribution functions and the transfer functions of the system are Fourier-Transform pairs. The Residence Time Distributions also provide valuable statistical insight as probability density distribution functions. The mean of the function is the average time a fluid element resides in the system. The calculated Residence Time Distributions correspond with our former findings. They also provide means to transfer the insufficiently slow permeation curves to sufficiently fast ones through convolution. Unfortunately, similarly to the results of **§1.** the Residence Time Distributions appeared also to be dependent on the sample materials gas permeation parameters.

V. Referred articles connected to the new results

[1]   Z. Filus, N. Tóth, G. Gulyás, T. Guba, G. Szabó, and Z. Bozóki, "Carrier gas flow arrangement based photoacoustic detection method for measuring gas permeability of polymer membranes," *Polym. Test.*, vol. 32, no. 6, pp. 1099–1104, Sep. 2013.

[2]   T. Guba, Z. Filus, K. A. Simon, G. Szabó, and Z. Bozóki, "Comparison of the accuracy of curve-fitting methods for the determination of gas permeability parameters of sheet polymer samples," *Polym. Test.*, vol. 46, pp. 59–64, 2015.

[3]   Z. Bozóki, T. Guba, T. Ajtai, A. Szabó, and G. Szabó, "Photoacoustic Detection Based Permeation Measurements; Case Study for Separation of the Instrument Response from the Measured Physical Process," *Photoacoustics*, Aug. 2018.