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# Quantification of binary mixtures of the freones R22 and R134a by surface plasmon resonance

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## Abstract

For the recycling process of freones a high purity of the analytes has to be guaranteed. A fast and inexpensive online monitoring is desirable. In this study the quantification of binary mixtures of the freones R22 and R134a by surface plasmon resonance (SPR) was studied using a self-built Kretschmann set-up. A microporous polycarbonate was used as sensitive layer. Due to a size dependent sorption and desorption kinetics of the two freones a quantitative characterization of binary mixtures is possible by the use of only one sensitive layer. 441 different binary mixtures for calibration and 400 test mixtures were measured over time. The measured signals were subdivided into points of time and used as input variables for the data analysis by neural networks. An optimization of the number and type of these points of time resulted in a small relative RMSE of prediction of 1.68% for R22 and 2.33% for R134a for the test mixtures.

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**Keywords:** Surface plasmon resonance (SPR); Freones; Polycarbonate; Neural networks; Multicomponent analysis; Time-resolved measurement

## 1. Introduction

For decades R22 has been widely used in refrigerators and air conditioners. Yet, the damages of the ozone layer caused by chlorofluorocarbons (CFC), like R22, are well known [1]. Consequently, they have been substituted by hydrofluorocarbons (HFC), which cause less damage to the ozone layer. Among these substitutes R134a is the most prominent representative [2]. Nevertheless HFCs are greenhouse gases. An economical procedure of recycling of these substances is desirable. For online monitoring of the recycling process an inexpensive and fast method is necessary. Thereby, a high purity of the freones has to be guaranteed. In this approach a single surface plasmon resonance (SPR) sensor is used to quantify binary mixtures of the freones R22 and R134a in a concentration range of the relative saturation pressure ( $p_i/p_{i0}$ ) 0 to 0.1.

SPR sensors have been described for various applications for the last two decades [3]. In 1982 the use of SPR sensors for gas detection was demonstrated by Nylander et al. [4]

and Liedberg et al. [5]. SPR-based sensors detect changes in the refractive index of the sensitive layer with a time resolution of a few seconds. In this study a microporous polymer is used as sensitive layer. The size selective effect of the micropores causes size dependent sorption and desorption kinetics of the two analytes [6]. The sorption and desorption of smaller analytes into the polymer is faster than the sorption and desorption of bigger analytes. Exploiting this effect a size selective quantification of different analytes is possible [7,8].

In this study the sorption and desorption kinetics of gases are observed by time resolved measurements using SPR. Short measurement times were realized by the use of an only 60 nm thick sensitive layer.

Pure analyte calibrations for R22 and R134a are performed and two data sets of binary mixtures of R22 and R134a are measured. The changes of the refractive index of the sensitive layer are recorded over time. The signals at definite points of time will be further referred to as points of time. These points of time are used as independent variables for a calibration by the use of neural networks. Finally the most important points of time of sorption and desorption are identified by a feature selection procedure resulting in an improved prediction.

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## 2. Experimental

### 2.1. Surface plasmon resonance

The SPR set-up used in this work was initially suggested by Kretschmann in 1968 [9]. In this set-up parallel-polarized white light (5 V/5 W krypton with integrated reflector, Welch Allyn, New York) is focused at a constant angle through a glass prism under total reflection conditions onto a silver film evaporated onto the glass (Fig. 1). The surface plasmons are excited at the back surface of the silver layer. The reflected light is coupled into a multimode fiber and detected by a diode array spectrometer (MMS Zeiss, Jena). The TE-mode is used as reference signal, as the surface plasmons are only excited by the TM-mode. On top of the silver film a sensitive layer is located. The resonance wavelength of the surface plasmons is influenced by the refractive index of the sensitive layer. Because of the high temperature dependence of the refractive index, the temperature has to be kept at a constant value by a thermo regulator (Julabo F34-MD) with a temperature constancy of 0.01 °C.

### 2.2. Coating materials and procedures

The silver was evaporated onto a glass prism (BK7, halfcylindric, ground 20 × 40 mm,  $n_D = 1.5168$ ) using a

vacuum evaporation system (Pfeiffer Vacuum GmbH, Wetzlar, Germany). Approximately 50 nm of silver was deposited onto the glass at a rate of about 1 nm s<sup>-1</sup> under high vacuum conditions (10<sup>-6</sup> to 10<sup>-7</sup> mbar). The thickness of the metal layer was monitored by a crystal oscillator.

The sensitive layer was prepared using 20 ml of a polycarbonate solution (Makrolon M2400, Bayer AG, Leverkusen Germany, 0.75 wt.%) in chloroform and toluene (3:1). The solution was spin-coated onto the silver surface (Convac 2001, Wiernsheim, Germany) for 40 s with 3000 rpm. The sensitive layer had a thickness of about 60 nm determined by a surface profilometer (Alpha Step 500, Tencor Instruments, Mountain View, USA).

The gas mixtures were generated using a gas mixing station with computer-driven mass-flow controllers (MKS, Munich, Germany). A four-way valve before the cell ensured that the path length was the same for all analytes. Dry synthetic air was used as carrier gas. All measurements were performed at a constant flow rate of 300 ml min<sup>-1</sup>.

### 2.3. Data sets

In addition to single analyte measurements, two multi-component data sets were recorded for the multicomponent analysis of binary mixtures. The first data set was a 21 level full factorial design whereby the relative concentrations of

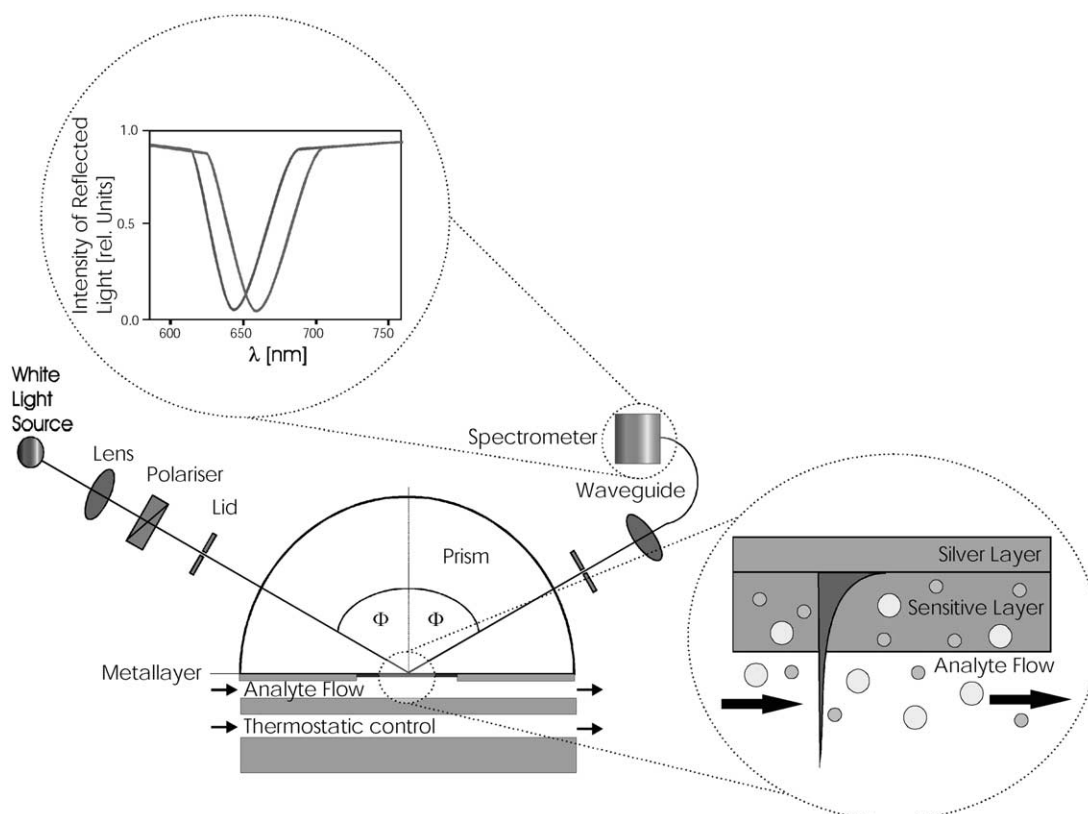


Fig. 1. Experimental set-up.

the two analytes were varied between 0 and 0.1  $p_i/p_{i0}$ . This data set was used for the training of the neural networks and for the feature selection. Further, it will be referred to as calibration data set. The second data set is a 20 level full factorial design and will be referred to as test data. The concentrations of this independent test data set were varied between 0.0025 and 0.0975  $p_i/p_{i0}$  in 0.005 steps. Thus all concentration levels of the two data sets are different and consequently the test data set should give a realistic estimate of the network performance in a real world situation [10]. In total 841 different mixtures of the two freones R22 and R134a were measured by SPR. All measurements were performed in random order.

The sensitive layer was exposed to the analyte–air mixtures for 60 s and afterwards to synthetic air for 300 s for recovery. During the sorption and desorption process, the signal was recorded with a resolution of 45 data points. The signals at each point of time were used as independent variables for a multivariate calibration by the use of neural networks. All data were autoscaled by subtracting the mean and by dividing by the standard deviation of each variable.

#### 2.4. Neural networks and feature selection

As there are numerous excellent textbooks available on neural networks [11–14] only a short overview of the neural networks used in this study will be given. The neural networks implemented belong to the class of the feedforward backpropagation networks. Separate nets were used for each analyte. The topology consisted of 1 output unit, 8 hidden units and as many input units as points of times used. The nets were fully connected. Hyperbolic tangent was used as activation function for the hidden layer and a linear activation function was used for the output layer. The training included a maximum of 2000 learn cycles. An advanced variant of Backpropagation was used as optimization algorithm, called scaled conjugate gradient (SCG) [15], which makes use of the pseudo-second-derivative information. In contrast to standard backpropagation, SCG converges faster, is more capable of dealing with local minima and is not sensitive to any parameters, which were all set to standard values suggested in [15].

Neural nets are often affected by an effect called overtraining [16]. This means, that a neural net learns an often too small calibration data set by heart instead of generalizing the data and consequently performs bad on new data like test data sets. The overtraining was anticipated by the so-called early stopping [17] and by a variable selection, which is also known as feature selection. Early stopping was implemented by stopping the training when the error of cross-validation of the calibration data starts going up, as the net may start loosing its generalization ability at this moment. A feature selection reduces the size of the network and helps to prevent the overtraining, since the number of training objects should be several times larger than the number of links of the network for an effective generalization ability [18].

For the feature selection a procedure was used, which is described in detail elsewhere [8]. Briefly, this feature selection is based on growing neural networks according to Vinod and Ghose [19]. The procedure starts with an empty network and inserts different network elements to reduce the error of prediction until this improvement is <3%. This procedure is repeated 400 times with different partitionings of the calibration data set into calibration and prediction data. Then the variables are ranked according to the frequency of usage in these 400 networks. Finally the variables are iteratively added to a final neural network in the order of the ranking, until a minimum of the error of prediction is reached.

In this study, the quality of prediction of the test data and the calibration data is judged by using the relative root mean square error of prediction.

$$\text{RMSE}_{\text{rel}} = \sqrt{\frac{\sum_{i=1}^N (\hat{y}_i - y_i)^2 / N}{\sum_{i=1}^N y_i / N}} \quad (1)$$

where  $N$  is the total number of data,  $\hat{y}_i$  the predicted concentration and  $y_i$  the true concentration.

All calculations were performed by a new implementation of the Stuttgart Neural Network Simulator [20,21] on a personal computer.

### 3. Results and discussion

#### 3.1. Pure analytes

In Fig. 2 the shift of the resonance wavelength of the surface plasmon is shown for both analytes. Due to the analyte exposure the refractive index of the sensitive layer increases and therefore the resonance wavelength increases. The microporous layer used is a glassy polymer with a mean size of the pores of 0.1 nm<sup>3</sup> [22]. The volumes of R22 (0.120 nm<sup>3</sup>) and especially R134a (0.140 nm<sup>3</sup>) are slightly bigger than the mean size of the micropores. The sorption of the analyte into the sensitive layer causes the replacement of the air in the micropores by the analyte and a swelling of the sensitive layer. This results in an increase of the refractive index and therefore the change of the resonance wavelength is also positive.

The sensitive layer was exposed to alternating sequences of synthetic air and various concentrations of the pure analytes between 0 and 0.1  $p_i/p_{i0}$ . The signal response for both analytes is fast and reversible and the signals of the two analytes differ in shape when recorded with a time resolved measurement. The sorption and desorption kinetics of smaller analytes into the glass polymer, in this case R22, is faster than the sorption and desorption kinetics of analytes with a bigger volume, like R134a (Fig. 2). The profile of the R22 curve is rectangular, which implies a very fast sorption and desorption kinetics of the analyte. For R134a the profile of the curve shows a curvature, which stands for slower interaction kinetics of the analyte with the polymer. As can be seen in Fig. 2 the signal to noise ratio of both analytes is

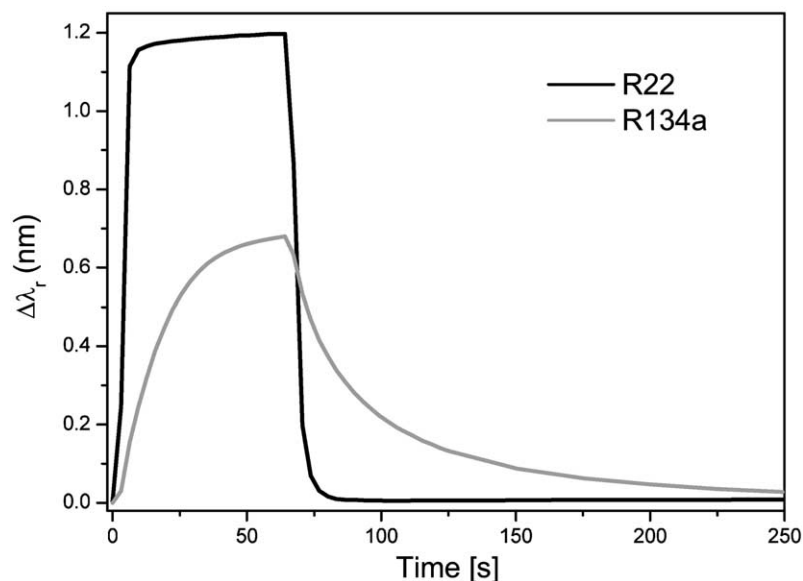


Fig. 2. Time-resolved measurements of the highest concentration of R22 (black) and R134a (grey).

quite high after an analyte exposure of 60 s. The signal of both analytes has returned to the baseline within 5 min.

In Fig. 3 the calibration curves after an exposure of 60 s of R22 and R134a are shown. The difference of the resonance wavelength between the exposure to synthetic air and exposure to analyte is recorded. The standard deviation of three measurements is represented by the error bars. The signals of R22 are higher than the signals of R134a because the saturation of the polymer layer with analyte is reached after 60 s of exposure to R22 but not for R134a, whereas a saturation is not necessary for the quantitative evaluation of the measured signal. The calibration curves show a curvature and can be explained by the limited number of

micropores. As the relationship between the concentrations of the analytes and the sensor responses is non-linear for both analytes, a non-linear method like a neural network is needed for the calibration of mixtures of both analytes.

It can be concluded, that a quantification of binary mixtures of R22 and R134a by this single sensor set-up should be possible by exploiting the different interaction kinetics of the two freones with the microporous polymer.

### 3.2. Mixtures of R22 and R134a

The neural networks were trained using the calibration data set and a subsequent prediction of the test data was

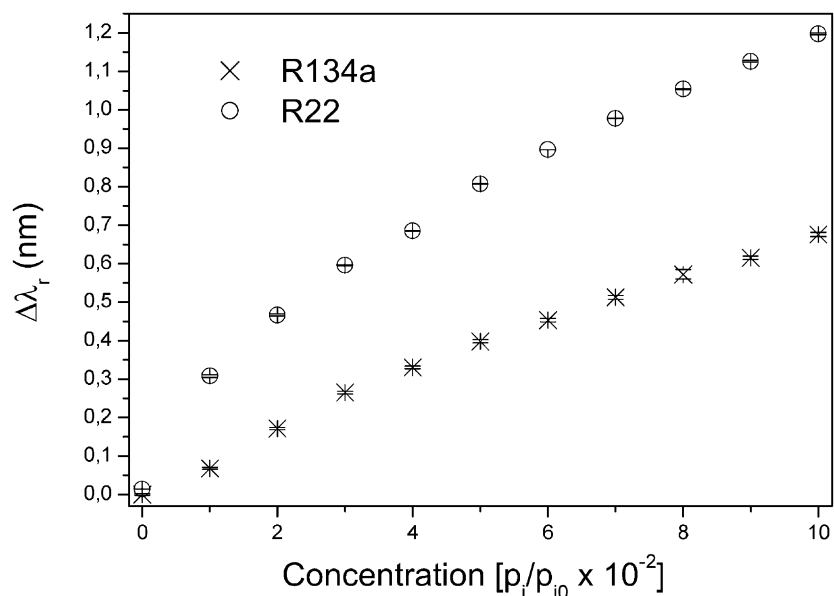


Fig. 3. Calibration curves for R22 and R134a. Signals are recorded after 1 min of exposure of the sensitive layer to analytes.

Table 1  
Relative RMSE (R22 and R134a) of the prediction of calibration and test data in % for networks using different points of time

Points of time	R22		R134a	
	Calibration	Test	Calibration	Test
45 (all)	1.49	1.89	2.49	2.86
13	1.34	1.68	2.23	2.33
7 (<30 s)	1.94	2.10	3.35	4.07

performed. First, all 45 points of time were used for the training of the neural networks. The relative errors of the cross-validation and of the prediction of the independent test data set are listed in Table 1. The concentrations of the test samples were predicted with a relative RMSE of 1.89% for R22 and 2.86% for R134a.

Though these quite low relative errors of the prediction of the test data demonstrate, that the neural networks using all 45 points of time show a good generalization ability, it is well known, that the inclusion of too many variables can cause several problems [23–28]. Noisy and redundant variables might be included, which hide essential variables, a high number of variables often prevents the iterative calibration of the neural networks from finding a good solution and last but not least many variables induce a big neural network with the problems of overtraining as already discussed in Section 2. To reduce the number of variables, a feature selection was performed. Thereby, the variables (points of time) are ranked according to the importance in a first step. The ranking is expressed as frequency of selection of a variable among 400 growing neural networks in Fig. 4. There are two time intervals, which are most prominent for the prediction of the compositions of the binary mixtures. The first time interval is located directly after the beginning of exposure to analyte and the second interval is located directly after the end of exposure

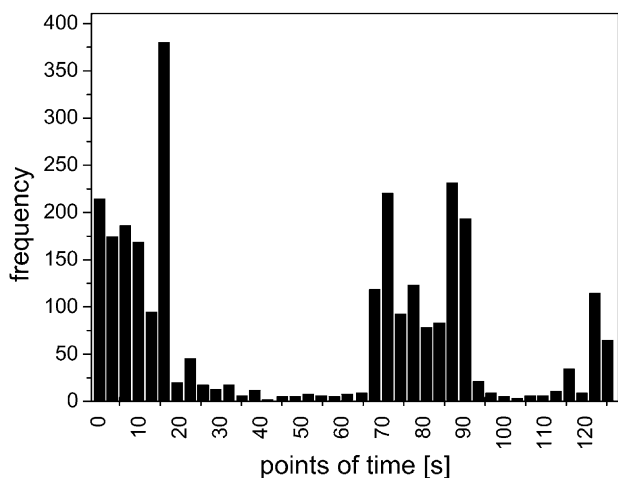


Fig. 4. Importance of the various points of time expressed as frequency of being selected during the feature selection process.

to analyte. Thus, the beginning of the sorption and the beginning of desorption process seems to be most important. In a second step, a neural net is built by adding the variables iteratively until a minimum error of prediction is reached. For this data set, the minimum error of prediction of the calibration data set was reached with a neural network using 13 points of times. These points are located in the first 20 s of exposure to analyte (3, 6, 9, 12, 15 and 18 s), directly after the exposure (71, 74, 77, 80, 90, 93) and at 125 s. The prediction of the neural network using these 13 points of time shows excellent results for the test data of 1.68% for R22 and 2.33% for R134a (Table 1). Consequently, the prediction of the test data, which were not involved in the feature selection process, is significantly better than the prediction of neural nets using all points of time. The differences of the errors between the calibration data and the test data are very small, indicating an excellent generalization ability of the neural networks.

The signals of the pure gases show a standard deviation of 0.20% for R22 and 1.26% for R134a. These variations are caused by the gas mixing station, by a varying measurement temperature and by noise of the spectrometer. The variations are also present in the measurements of the mixtures and therefore the small increase of the relative errors for the calibration and prediction compared with the standard deviation of the signals of pure analytes shows the possibilities of the calibration by neural networks.

The results of the prediction using 13 points of time can be graphically presented in so called true-predicted-plots. In these plots the concentration predicted by the neural networks is plotted versus the true concentration of the component. As the predictions of the 441 calibration data and 400 test data cannot be graphically resolved, the predictions are represented by the mean and standard deviation of each concentration level.

In Fig. 5a the true-predicted-plots of the cross-validated calibration data are shown and in Fig. 5b the true-predicted-plots of the test data are demonstrated. The standard deviations of all predicted concentrations are very small but are growing with the concentrations. The means of practically all concentration levels are located on the diagonal, demonstrating the absence of a bias, except of the absence of R134a in the calibration data, which is predicted as 0.0015.

A drawback of the time-resolved measurement is the need of time before a prediction can be made. For example, the prediction using 13 points of time needs 125 s of measurement for an evaluation. Thus, for the sake of a reduced measurement time, only the signals of the first 30 s of analyte sorption into the sensitive layer were used for the quantification of the binary mixtures. With this approach, the concentrations of the test samples were predicted with a relative RMSE of 2.10% for R22 and 4.07% for R134a (Table 1) using 7 points of time. The errors are significantly higher than the errors of neural nets using 125 s of measured signals. When reducing the exposure to analyte to 30 s and using additionally the first few seconds of desorption for an



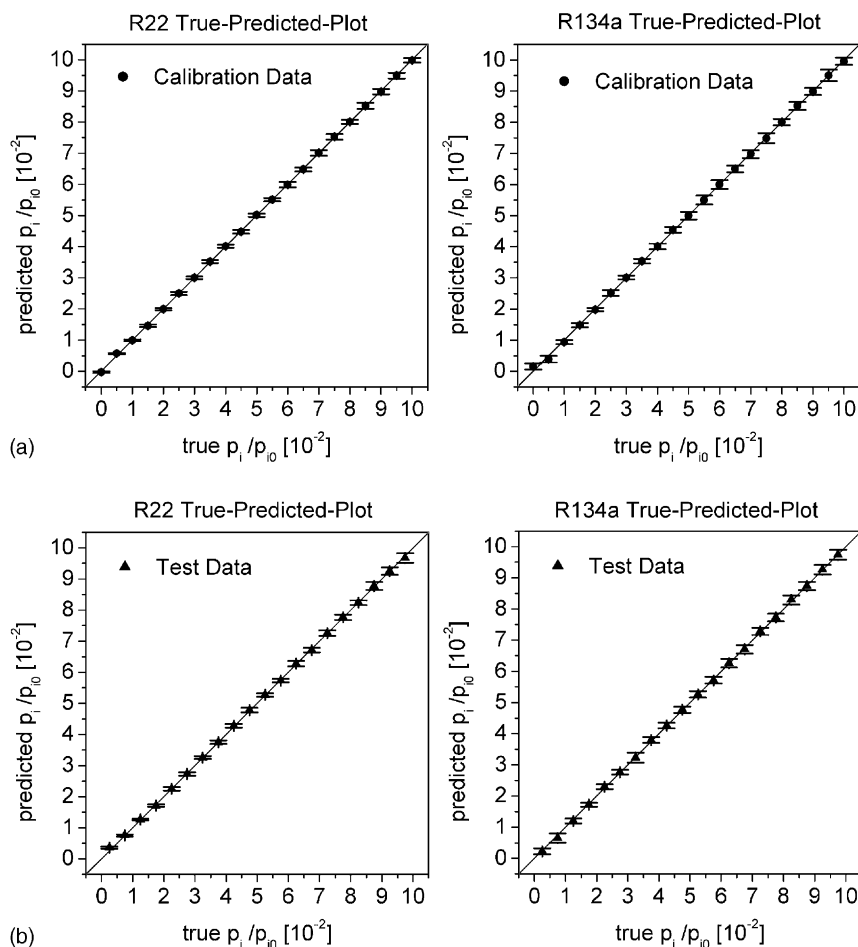


Fig. 5. (a) Predicted concentrations of the calibration data set versus the true concentrations of the binary mixtures (expressed as relative pressure). (b) Predicted concentrations of the test data set vs. the true concentrations of the binary mixtures (expressed as relative pressure).

accelerated online-monitoring, the errors of prediction are expected being between the errors of neural nets using 125 s of signal and neural nets using 30 s of signal. Thus, fast measurements would be possible with acceptable errors. By using shorter exposure times the recovery time between two measurements could also be shortened as the desorption of R134a would need less time to be completed.

#### 4. Conclusions

It has been shown that the quantitative characterization of binary mixtures of the freones R22 and R134a can be realized by surface plasmon resonance spectroscopy using a microporous polycarbonate as sensitive layer. The sorption and desorption of the two freones into the micropores of the polymer is fast and reversible. The kinetics for both analytes differ enough for a quantification of binary mixtures by the use of only one sensor. The combination of a thin sensitive layer, the time resolved measurement and the data evaluation by neural networks shows excellent results. The RMSE of 1.68 and 2.33% are very low, respectively, and the

measurement time is short enabling an installation of such a set-up in sensing stations for an online monitoring of the recycling process.

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## Biographies

*Stefan Busche* graduated at the University of Tuebingen in 2002 (Master of Chemistry). He has started working on a PhD Thesis now. He is experienced in gas sensing using SPR as detection principle.

*Frank Dieterle* graduated at the University of Tuebingen in 2000 (Master of Chemistry). Currently, he is working on a PhD Thesis on the fields of chemometrics and bioinformatics. He is experienced in multivariate calibration by the use of neural networks and genetic algorithms.

*Birgit Kieser* studied chemistry at the Universities of Tübingen and Dijon and was awarded her diploma in 1998. She received the doctoral degree in physical chemistry in the group of Prof. Gauglitz at the University of Tuebingen in 2002, working on the detection of VOCs and gases by means of optical sensors, especially SPR.

*Günter Gauglitz* is a professor in the Institute of Physical and Theoretical Chemistry at the Eberhard–Karl–University of Tuebingen since 1987. He received his Master of Science in 1966, at the State University of Iowa, and his PhD Degree in 1972, at Tuebingen, Germany. At present, there are more than 20 PhD and Master students in his group, working in the development of various types of optical detection principles for chemical and biochemical sensing, such as reflectometric interference spectroscopy, surface plasmon resonance, integrated optical Mach–Zehnder devices, total internal reflection fluorescence, and fluorescence resonance energy transfer. Polymers and biomembrane surfaces are applied to the detection and quantification of molecular and biomolecular interaction, such as the measurement of volatile organic compounds in combination with various methods of multivariate data analysis. Antibody and antigen interaction is used for the quantification of pesticides and estrogens, and recently DNA and protein interaction were added providing methods for high-throughput screening, genomics and proteomics.