Quantification of Binary Mixtures of the Freones R22 and R134a by Surface Plasmon Resonance

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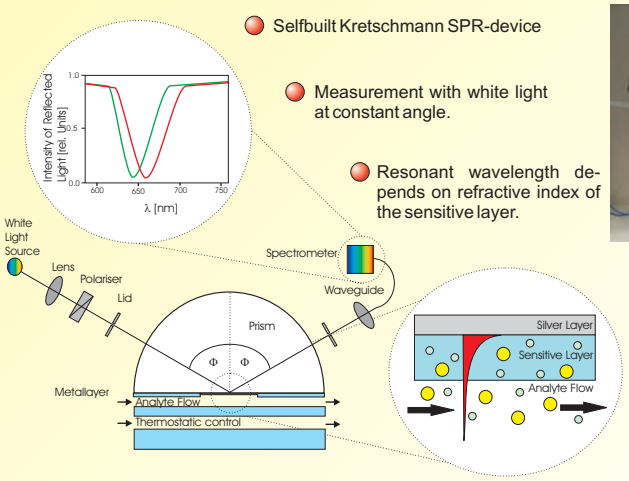
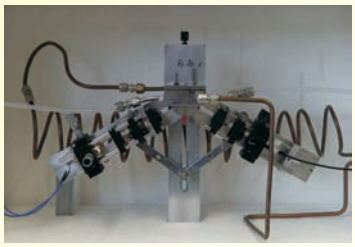
Introduction

- Chlorofluorocarbons cause damage to the ozone layer. The goal of this work was the detection of R22 in the vapour of R134a using Surface Plasmon Resonance.
- A single sensor set-up was used for the multi-component analysis. The temporal information of the sensor is evaluated.
- A microporous polycarbonate was used as sensitive layer. The thicknes of the sensitive layer was varied between 60 and 300 nm.
- The sensor response during analyte sorption and desoprtion was time-resolved evaluated by neural networks. Some hundred binary mixtures of R22 and R134a were measured by SPR.

Instrumental Set-up

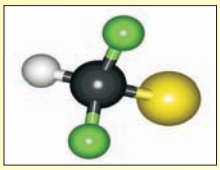
- Selfbuilt Kretschmann SPR-device
- Measurement with white light at constant angle.
- Resonant wavelength depends on refractive index of the sensitive layer.



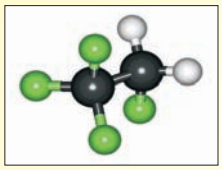


- Changes in the refractive index can be detectected as a shift of the absorption-minimum.
- Detection of the absorption-minimum by spectrometer.
- The time needed for a measurement depends on the thickness of the sensitive layer.

Analytes

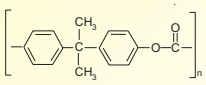


R22
Difluorochloromethane



R134a
1,1,1,2-Tetrafluoroethane

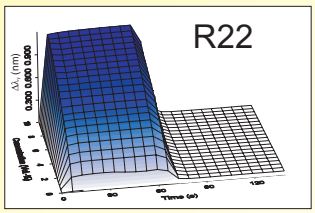
Sensitive Layer

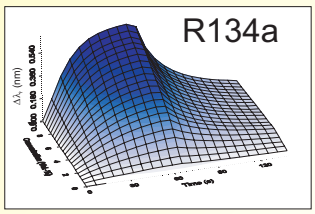


Polycarbonat Makrolon®
Makrolon M2400, Bayer AG,
Leverkusen, Germany

Microporous polymer:
median pore diameter
0.1 nm

Calibration

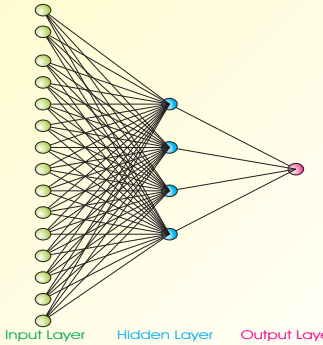




- Thickness of the sensitive layer: 60 nm
- Calibration of both analytes between 0 and 10 percent by volume.

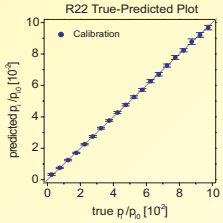
Data Evaluation

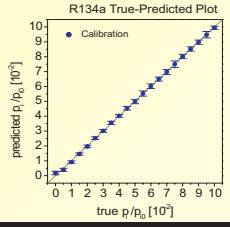
- Input variables were centered and standardized
- Output variables were scaled from -0.9 to 0.9
- One neural net per analyte
- Activation functions of units: tanh
- Training algorithm: Rprop



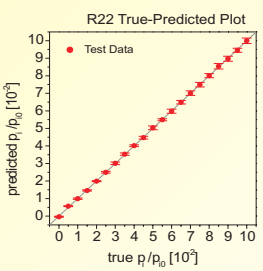
Results

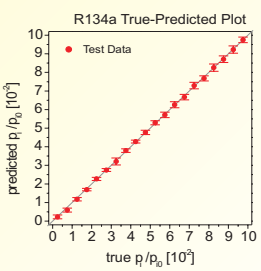
441 different mixtures as calibration-set
Each mixture was evaluated by 21 neural nets





400 different mixtures as independent test samples
Each mixture was evaluated by 21 neural nets





Relative Error:

	Median Cross-Validation-Error	Median Test-Data-Error
R22	2.6 %	2.2 %
R134a	3.6 %	3.0 %

Summary and Outlook

- By the variation of the layer thickness the measurement-time can be reduced to 60 seconds of analyte exposition.
- Short measurment times can be realised.
- The results show that detection of the two analytes with only one sensor can be realised very good.
- The Prediction of 400 independent test mixtures (not used for calibration) was very exact for R22 and R134a.
- A high purity of R134a can be guaranteed.
- Measurement of other small analytes with the same instrumental set-up is possible.