

*Original papers***Cholesteric liquid crystals for solvent vapour detection –
Elimination of cross sensitivity by band shape analysis
and pattern recognition**

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Abstract. Cholesteric liquid crystals are suitable as sensitive materials for the detection of solvent vapours, such as aromatic and halogenated hydrocarbons. The optical properties of these materials are determined by their molecular short range order, given by the so-called pitch which is influenced by analyte incorporation. Thus, the wavelength of the absorbance band is shifted and the sensor effects are followed in the visible range at a defined wavelength on the flank of the band. Even a variety of aromatic or halogenated solvents, e.g. tetrachloroethylene, can be detected in the ppm-range. By using the whole spectral information combined with partial least squares analysis a separation of solvent effects from that of the disturbing temperature is achieved. Furthermore, these spectral data allow the optimization of the detection of halogenated hydrocarbons whereas the cross sensitivity to other analytes can be diminished.

Introduction

The gas phase detection of unpolar solvents such as halogenated or aromatic hydrocarbons is of great environmental interest and especially work place monitoring has rising economic importance. Due to the lack of a pronounced functionality of these analytes, such a detection is a delicate task [1]. Therefore, the analyte incorporation in ordered phases [2] such as cholesteric liquid crystals (LC) [3] seems to be reasonable since the short range ordering forces within the liquid crystal have a similar nature as the interactions between analyte and LC.

Cholesteric LCs can be described as anisotropic fluids characterized as an intermediate state between the solid phase and an isotropic liquid [4]. The single LC molecules are ordered in a helical arrangement which yields the unusual optical properties of these materials, such as the

dependence of colour on the observation angle [5] and temperature [6]. This behaviour is caused by an interaction of light waves with these molecular helices, that yield an optical grid with the respective interference phenomena [7]. The helices are characterized by their periodicity, the so-called pitch [8, 9]. The incorporation of solvent vapours into these anisotropic phases is accompanied by a change in the pitch height [10, 11] and therefore LCs can be used for the design of sensitive layers. This finding is either explained by altering the twisting angle between the single molecules or by compressing or stretching the molecule arrangements along their helical main direction [12].

Mixing different cholesteryl esters allows the tuning of the optical characteristics in a far range, so that the absorbance maximum can even be shifted in the visible range, e.g. to a wavelength of 820 nm as shown by a typical spectrum in Fig. 1. With respect to a technical application this spectral range is favourable due to the availability of cheap and suitable classical LEDs or laser diodes. In order to use cholesteric LCs in sensor systems a material optimization in terms of reducing environmental influences, e.g. temperature or relative humidity [13] have to be achieved. Electronic compensation methods or intelligent data interpretation [14, 15] offer possibilities to obtain smart sensors.

Experimental*Measurements*

The optical absorbance of the sensor layers was measured with a UV-VIS spectrometer (Perkin-Elmer, Lambda 2) under defined varying conditions concerning temperature, relative humidity and solvent concentrations. Thermostating was ensured by using an optical cell with an integrated temperature control of the measuring equipment as well as the test gas. The stream of air containing humidity and analyte vapour was mixed by mass flow controllers (Tylan FC 260). The time dependent characteristics are recorded at a defined wavelength at the point of inflection of the absorbance peak to give

Dedicated to Prof. Dr. Gerd Wedler on the occasion of his 65th birthday

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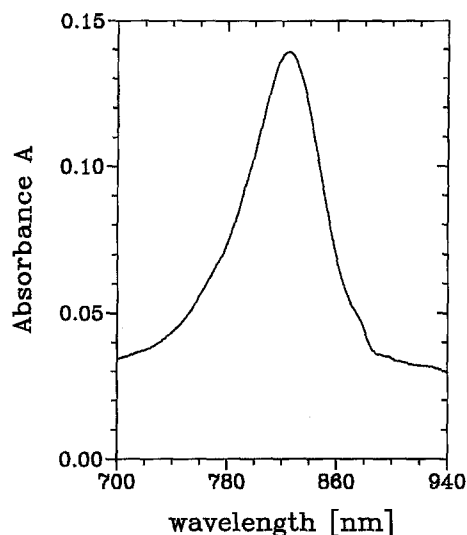


Fig. 1. VIS-spectrum of a cholesteric mixture (CC:CN:CO = 10:16:18-weight ratio) at 20 °C

optimized sensor signals. For the multiple wavelength observation the whole optical spectra were continuously recorded and finally software interpreted.

Sensor layers

The mixtures of the cholesteryl esters were obtained by heating the mixtures above their clearing points to a temperature of 110 °C. Cooling down to room temperature gives a homogeneous cholesteric phase which was applied as coating in the μm range on a styrene plate followed by a controlled spin-off process with a centrifuge as described earlier [16].

Chemicals

Cholesteryl chloride (CC), cholesteryl oleylcarbonate (CO) and cholesteryl nonanoate (CN) were obtained from ALDRICH. These compounds are described to form cholesteric phases at higher temperatures. Mixtures of these compounds in varying ratios yield materials showing the described optical properties in the visible range even at room temperature.

Results and discussion

Solvent sensitivities

The influence of halogenated and aromatic hydrocarbons on the optical absorbance of cholesteric liquid mixtures was tested. Furthermore, we studied the cross sensitivity of these cholesteric mixtures to humidity which is an omnipresent varying environmental disturbance. For these measurements we selected the carcinogenic tetrachloroethylene as analyte, which is very important due to its use in dry cleaners and has to be detected down to concentrations in the ppm range. The sensor character-

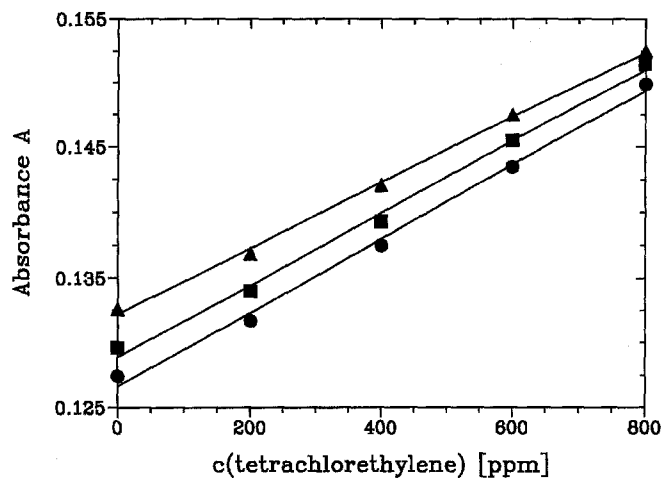


Fig. 2. Sensor characteristics of a cholesteric liquid crystal-absorbance A at 855 nm versus concentration of tetrachloroethylene in air at 20 °C for different degrees of humidity (CC:CN:CO = 10:16:18-weight ratio) (● = 10% RH, ■ = 30% RH, ▲ = 50% RH)

istics of the cholesteric mixture, given in Fig. 1, are shown in Fig. 2. A linear sensor behaviour is observed even up to concentrations of 0.1%. Especially the excellent reversibility, fast response times below one minute and the high sensitivity of this sensor material should be mentioned. Compared to the spectrometer noise the detection limit is less than 10 ppm tetrachloroethylene. The high sensitivity of such an optical sensor system is only comparable with highly mass sensitive SAW devices at high frequencies in the MHz or GHz range [17]. Results for another cholesteric mixture are given in Fig. 3. Chloroform shows a steeper sensor characteristic compared to benzene, since the bulky tetrahedral geometry of chloroform more strongly disturbs the anisotropic phase than the flat benzene molecule.

A common problem is the fact that most chemical sensors are not selective to a distinct solvent. Cholesteric liquid mixtures show different sensor characteristics to solvents belonging to different chemical parent compounds. To obtain more detailed information about this phenomenon we analyzed the spectra at different wavelengths. The sensor characteristics at two wavelengths (398 nm and 373 nm) on both sides of the absorbance maximum are shown in Figs. 4 and 5. While for example in a concentration up to 0.4% solvent vapour in air, methanol leads to no sensor effect, chloroform as well as tetrahydrofuran causes variations to the helical structure of the cholesteric liquid crystal (Fig. 4). In Fig. 5 it is shown that only chloroform gives a remarkable change in the absorbance, whereas methanol and tetrahydrofuran cause negligible effects. This finding is a remarkable advantage, since alcohols are often accompanying substances of chlorinated hydrocarbons, used in dry cleaners.

Temperature as interference factor

In contrast to other sensors, such as pellistors and semiconducting metal oxides [18], cholesteric LC sensors

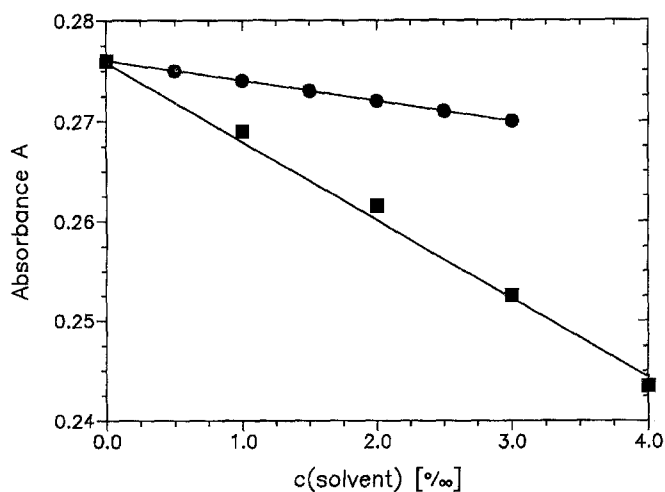


Fig. 3. Sensor characteristics of a cholesteric liquid crystal-absorbance A at 464 nm versus solvent vapour concentration in air at 20 °C (CC:CN:CO = 10:20:20-weight ratio) (● = benzene, ■ = chloroform)

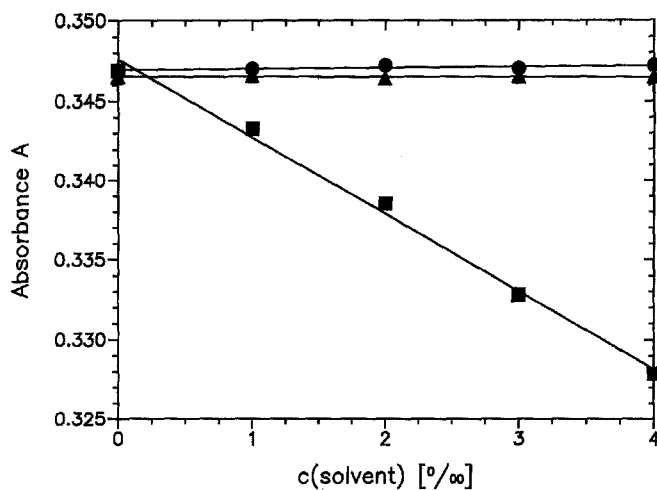


Fig. 5. Sensor characteristics of a cholesteric liquid crystal-absorbance A at 373 nm versus solvent vapour concentration in air at 20 °C (CC:CN:CO = 3:16:12-weight ratio) (● = methanol, ■ = chloroform, ▲ = tetrahydrofuran)

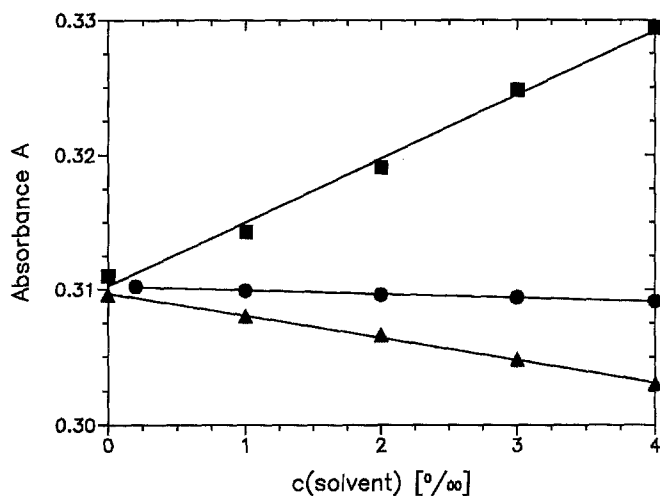


Fig. 4. Sensor characteristics of a cholesteric liquid crystal-absorbance A at 398 nm versus solvent vapour concentration in air at 20 °C (CC:CN:CO = 3:16:12-weight ratio) (● = methanol, ■ = chloroform, ▲ = tetrahydrofuran)

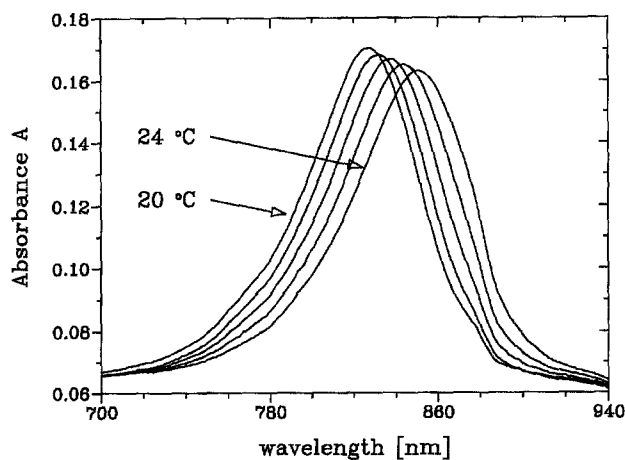


Fig. 6. Absorbance spectra-temperature dependence of a cholesteric liquid crystal (CC:CN:CO = 10:16:18-weight ratio)

can operate at room temperature. But a problem of these systems is their temperature dependence due to an influence to the pitch of cholesteric LCs and consequently their optical properties. Therefore, a temperature compensation is necessary.

As shown above analyte recognition is achieved by using the whole spectral data. The influence of temperature to the absorbance band of LCs (Fig. 6) is now tried to be interpreted as an additional analyte. Therefore, recording the absorbance at different wavelengths yields a set of data which resembles the answers of an array of sensors of different sensitivities and tuned selectivities. There are some mathematical methods to extract the contained excess information given by such a sensor array. The simplest method treats the data by a multiple linear regression (MLR) algorithm. The arising problems, in terms of collinearity, have been sufficiently described

[14]. A much more convenient method is given by the so-called principal component analysis (PCA) or the partial least squares (PLS) [19] method. Mathematically spoken, the information gained at n different wavelengths (n sensors) defines a sensor in an n -dimensional space. The aim of PCA is to find a new system of coordinates which describes the data in a way that the different data clusters lie on the respective different axes separated from noise and other disturbing influences. This allows not only the determination of the concentrations applied from the answer pattern but eliminates the problems due to collinearities in the data set when using the MLR method. For the PCA the non-linear iterative partial least squares (NIPALS) algorithm is used. This is a recursive routine which yields a set of orthogonal principal components, with few axes containing high variance, corresponding the concentrated chemical information. This extraction of

the latent chemical information is a major advantage compared to the MLR method. The more sophisticated two-block-PLS method combines two principal component analyses for the input (concentrations) and the output (sensor answers) data.

Thus, in an ideal case the influence of temperature is transformed to one axis and each solvent of a measured mixture to an individual axis. There is also a set of axes which contain the noise and e.g. non-linearities of the sensor characteristics. In a practical application a total separation is only possible in few cases, but satisfying recognition abilities are achievable. The weight of the data relative to the new coordinates is increased compared to the original system. Resulting axes with low variance can be ignored, which leads to an elimination of noise. But care has to be taken that no relevant data are neglected.

To determine the optimum number of the so-called main components, the new set of axes and sensors, a model with three quarters of the data set is calculated. The remaining part of the data is not taken into account. The obtained model is then applied to the left out data, varying the number of principle components. This procedure, called cross validation, is carried out until all data are ignored for one time. In our case PLS is used for a band-shape and a band-shift analysis. The chemical interpretation is given by some examples.

It has been shown that rising temperatures cause a linear shift of the band maximum to longer wavelengths which is combined with a reduction of the observed sensor absorbance. The shape of the absorbance peak is independent of the temperature. A temperature raise of about 0.1 °C leads to a shift of 0.7 nm to higher wavelengths (Fig. 6). On the other hand, tetrachloroethylene in a concentration of 100 ppm in air causes a shift of the absorbance maximum of 2.5 nm, as given in Fig. 7, accompanied by a non-symmetric band shape deformation. Eight different wavelengths between 760 nm and 850 nm were used with the partial least squares analysis and yield a model system which shows the desired data separation. The applied algorithm is able to reduce the necessary information from eight dimensions to five independent variables. The calculated parameters and the real measured data are given in Table 1.

It can easily be seen that by the use of partial least squares analysis a separation between temperature and solvent concentration is achieved. The absolute error for the determination of tetrachloroethylene is in the region of some ppm. Combining a temperature measurement with our equipment, more accurate information will be gained. Noise will be eliminated and even unknown analytes or disturbances can be separated from the relevant concentrated information.

Sensor stability

In addition to temperature compensation problems the absolute stability of sensor materials is an important criterion for their practical use. Particularly their sensitivity to oxygen and light exposure should be low. Com-

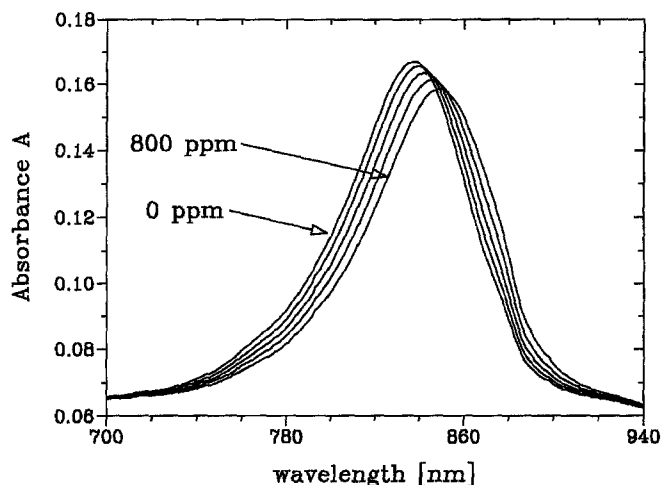


Fig. 7. Absorbance spectra-dependence on the tetrachloroethylene concentration of a cholesteric liquid crystal at 20 °C (CC:CN:CO = 10:16:18-weight ratio)

Table 1. PLS band shape analysis at eight wavelengths at varying temperatures and tetrachloroethylene concentrations

Real values		Results of PLS-analysis	
Temperature	Tetrachloro ethylene	Temperature	Tetrachloro ethylene
20 °C	200 ppm	19.93 °C	204.5 ppm
21 °C	400 ppm	21.01 °C	389.6 ppm
21 °C	600 ppm	20.99 °C	611.2 ppm
23 °C	800 ppm	22.98 °C	820.5 ppm

pared to highly coloured dyes [16], which can be also applied as sensor materials, LCs are favoured by a drastically enhanced photostability, since the colour of cholesteric liquid crystals results from a physical phenomenon. No electronic stimulations of the molecules to excited reactive states occur, which might lead in consequence to a destruction of the sensitive layer.

Conclusions and perspectives

Cholesteric liquid crystals as sensitive layers are a consequent development step combining the high sensitivity known from earlier optical sensor systems [16] with an extreme photostability. Thus, detection limits in the ppm range for analytes, such as aromatic and halogenated hydrocarbons are accessible. Furthermore these materials allow an easy tuning of the optical properties by varying the mixing ratio of the alkylester components. Especially with the multiple wavelength analysis of the absorbance an analyte recognition and a temperature compensation is realized. Even new perspectives are accessible, when applying new methods instead of the PLS algorithm, such as fuzzy logic [20] or neuronal nets [21], [22], [23]. Using integrated optics [24] miniaturized intelligent sensor systems which are small as a pocket calculator can be designed for a huge field of applications.

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