OPTICAL SENSORS
DO THEY REQUIRE A COMPUTER?

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SUMMARY

Recently, optical sensors have obtained increasing interest in application and research. In principle, they are considered to detect selectively compounds in analyte mixtures by their specific activity of the chemicals or biochemicals in the sensor head. But, evidently this requirement cannot be fulfilled at the moment. For this reason, in addition to the use of microprocessors for the automatization of the sensor measurement, computers have to be used in the evaluation of data to increase selectivity by the use of sensor arrays and methods of multicomponent analysis and pattern recognition, respectively. The necessity of computers in the physico-chemical characterization of the sensor material, in the process control, and in the data evaluation is demonstrated. Furthermore, some examples of sensors based on fiber optics and interferometric detection principles as well as waveguide applications are discussed.

PRINCIPLES OF SENSING

In physical, quantum, and technical chemistry computers have been applied for many years either to process control, evaluation, or number crunching. Computers are understood as tools in natural sciences. For this reason, any paper dealing with the application of computers can not just report an increase in the rate of data handling but must point out the novelty either of the algorithms used or the physico-chemical question applied to. The ability of modern computer equipment allows to visualize numerical calculations. Therefore the presentation of simulation curves together with experimental data has turned out to be a typical improvement for the scientist. For this reason modern applications of computers use highly sophisticated equipment for measurement, take advantage of interactive graphics, and demonstrate the improvement in the solution of physico-chemical problems.

In recent years physical and analytical chemists have gained interest in the research on sensors. For this reason this topic is chosen to demonstrate the advantages of com-

puters applied in process control, data acquisition, graphical presentation, and numerical evaluation. The continuous measurement of analytes" concentrations in flow systems has been done for many years. In these applications sensors are considered to substitute the former equipment.

A sensor is defined to be an element or system which allows to monitor the concentration of an analyte or any physical parameter continuously and reversibly. Reversibility and continuity distinguishes sensors from taking probes or spectra conventionally in flow sytems. Besides, a sensor element is considered to be a comparatively simple device. For better understanding: no one would consider a mass spectrometer or a gas chromatograph to be a sensor, even though they will be able to detect selectively different components in analytes. On the other hand, an electrode will represent a typical sensor element.

In general, one distinguishes between electrochemical and optical sensors. The later ones will transform the optical signal into an electrical one in a second step. Combining the "optical" method of monitoring and the term "electrode", the new term "optode" [I] and in the Anglo-Saxon society the term "optrode" [2] were introduced. Recently, at least in Germany, the term "optode" is favoured. Sensors are typically applied to process control in the production of pharmaceutics and in chemical factories. Another large field of application is going to be environmental analysis, controlling the quality of water and atmosphere.

The type of optical sensors dealt with here differs from those used in robotics or as light gates. The idea is to use a sensor system to monitor selectively a single component in a multi-component system. The selectivity is intended to be achieved by the material of the sensor element. The chemicals - or better biochemicals - used are supposed to react specifically with the interesting component without cross-interferences by the other components in the analyte. In this case, the sensor element is going to result the intended distinction. Up to now, only a few specific chemical reactions have been detected and could be applied to analytics. A combination of those in an array of sensor elements would result the desired selective quantitative determination of many components simultaneously. This device is not achieved yet.

Another possibility is to take biochemicals. They are considered to be more specific. The idea is to utilize either enzyme reactions or antigen-antibody-interactions. But this material lacks the stability exposed to typical real analytes and to the measurement radiation. For this reason the state of the art is to use many sensors in an array. Its elements only show a different sensitivity to the analyte's components. The signals obtained for the different sensors give a weighted summation of informations. This fact allows to answer the stated question in the title whether sensors need a computer. They turn out to be necessary for data analysis using either multi-component analysis or pattern recognition methods.

COMPONENTS OF OPTICAL SENSORS

An advantage of optical sensors is the possibility of spectral detection. Other advantages are listed elsewhere [3]. In short they can be summarized: to get multidimensional data arrays, to avoid disturbances by external electromagnetic fields as well as explosions by electric sparks, and to give the chance to use internal standards. Thereby continuous stability control and the correction of drifts becomes possible.

Optical sensor systems consist of the sensor head, a light source, fiber optics, a detector, and a unit for signal processing and computing. In the case of chemical or biochemical sensors the sensor head contains the receiver (for the specific (bio-)chemical reaction) and normally a transducer which indicates the reaction. Interaction of the sensor head with the analyte causes for example a color change of an indicator dye (transducer) produced by the pH-change during an enzymatic reaction (receiver). Further examples are swelling effects in polymers by up-taking gases and effecting the refractive index at the sensor head. Another application is the quenching of fluorescence by gases.

The fiber optic transports the radiation of a light source (laser, mercury-, xenon-arc, or tungsten lamps) to the sensor head and the resulting optical signal to a detection system. These fiber optics are in most cases bifurcated. The detection unit contains a photodiode for monochromatic detection and linear photodiode arrays or even CCD cameras in the case of spectral detection.

INTERFACE CHARACTERIZATION BY ELLIPSOMETRY

The interaction between sensor-head and analyte depends on its physico-chemical properties. Modern instrumental techniques in surface and interface examination can be used to understand these interactions. These methods need computer or microprocessor assistance. A modern optical tool is ellipsometry [4]. It allows to obtain optical information about the surface of the sensor head and any mono- and multi-layer interfaces. Linearly polarized light is sent to the surface and the reflected beam is analyzed in dependence on wavelength with respect to the angle of polarization and the phase difference. The amplitude of the reflected two beams (parallel and perpendicular to the optical normal) depends on all the optical constants of the surface material, the properties of the monolayer, and the thickness of this layer. The information is included in two angles $(\tan \psi, \cos \Delta)$. In fig. 1 their dependence on wavelength is given as the result of a measurement of a silica layer on silicium substrate using an angle of incidence of TO.2°.

These measured data are compared with the results of simulations using Fresnel's equations. It becomes obvious that a small change in the silicium dioxide layer of 0.1238 μm

to 0.1225 |im gives an observable difference between the measured and the simulated curves [5]. Of course, this simulation requires some efficient computer equipment and some skillness in programming. Commercial software is only available for some stand-ard layer-systems.
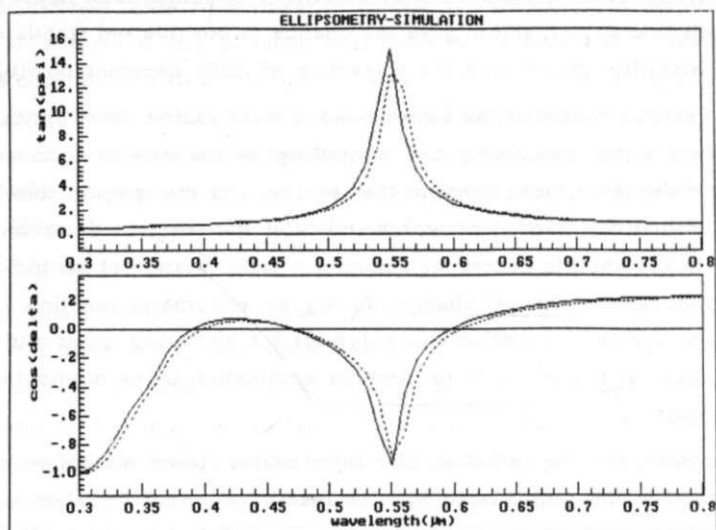

fig. 1: Ellipsometry curves measured and simulated with good parameters (———),
(....) wrong parameters

SENSORS USING TRANSM1TTANCE, FLUORESCENCE, AND INTERFERENCE

In fig. 2 an instrumental set-up is shown containing a flow cell, the sensor head, fi-ber optics, a light source, a linear diode array detector, and a computer. The appara-tus can be used either to measure the fluorescence of some labelled lipo-peptides [6] or the reflectance (transmittance) of sensor heads containing urease and the indicator dye phenol red [T,8]. Another approach is an interferometric measurement of a poly-mer layer placed on a quartz or glass platelet and exposed to hydrocarbon gases or liquids. In Fig. 3 the schematics of the polymer layer and the radiation geometries are given.

Light falling onto this multilayer system is partially reflected at each interface. The different reflected beams can interfere if the condition of coherence is fulfilled (thick-ness of the layer somewhat between 0,5 - 50 |im). The two partial light beams I_1 and I_2 will interfere in dependence on the phase jump 8 (for an electromagnetic radiation passing the interface from low to high optical density), the angle of incidence a, the refractive index n_2 (X) of the polymer, and the physical thickness of the polymer, with the following phase difference:

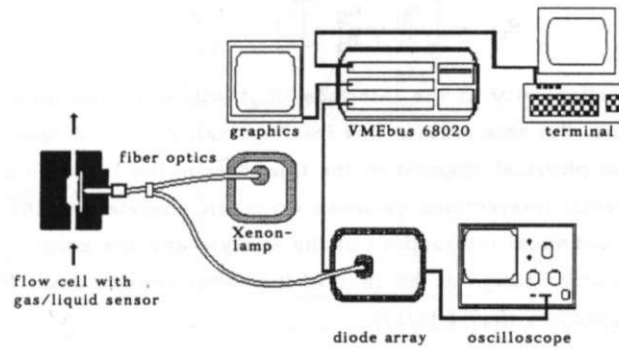$$\Delta = 2d\sqrt{n_2(\lambda)^2 - \sin^2\alpha} + \delta \qquad (1)$$

fig. 2: Set-up for reflectance, fluorescence and interferometric measurement.
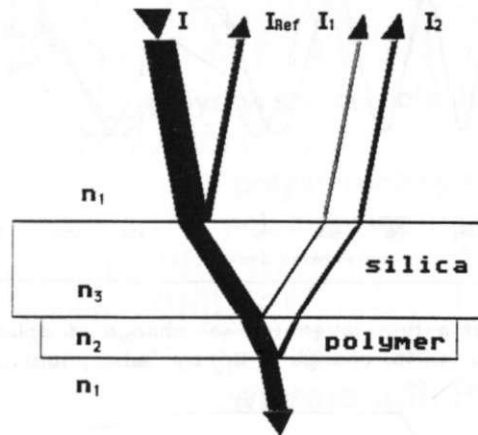

fig. 3: Polymer layer beneath a glass plate, pathways of radiation.

Taking one wavelength, this phase difference Δ of the partial beams will cause either a constructive or destructive interference. Observed is either high or low intensity. If polychromatic radiation is used, the different interferences at the different wavelengths will result an interference spectrum (fig. 4) [9,10].

The change in intensity with wavelength can be approximated by the following equation [11]:

$$I(\lambda) = I_1 + I_2 + 2\sqrt{I_1 \cdot I_2} \cdot \cos 2\pi\left[\frac{2n_2(\lambda)d}{\lambda} + \delta\right] \qquad (2)$$

In principle the distance between proximate extrema is influenced by $n_2(\lambda)$ and the physical thickness d (fig. 4(a/c)). Because of

$$I_2 \cdot R_{12} \left[I_{Ref} - I - I_1 \right] \tag{3}$$

and

$$R_{12} \cdot \left[\frac{n_1 - n_2}{n_1 + n_2} \right]^2 \tag{4}$$

$$>a \cdot {}_{R}12 \; []^*., \; - I \; " \; II] \tag{«}$$

and

any change of the reflectivity at the interface (R_{12}) will vary the amplitude of the reflected beam I_2, too. For this reason, this interferometric method also allows very sensitively to monitor physical changes in the thickness of the layer, to observe optical changes by physical interactions between up-taken analyte and the polymer, to measure physical or chemical interactions of the analyte and the polymer in the layer, and to determine any change of the ratio of the refractive indices at the interface by physi- or chemisorption Cfig. 4 Ca/b)).
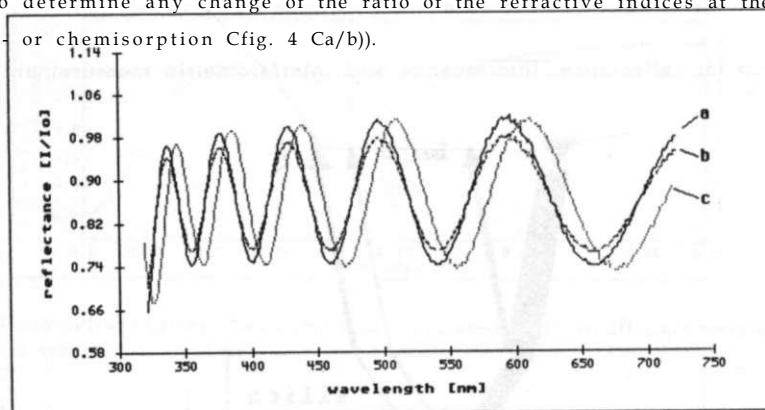

fig. 4: Interference spectra at a thin layer: (a), (c) change of optical pathlength 2dn₂CX) acc. to eq. (1), (a), (b) change of R_{12} by "adsorption" influencing the amplitude acc. to eq. (2).

Organic gases or liquids passing the sensor head will penetrate into the polymer film and cause a change in the interferometric pattern Cchange in fig. 4, curve a —> c) by swelling of the siloxane polymer. This amount of swelling depends on the property of the gas and the type of polymer used (polymerized thermally or photochemically) [10,12] Csee table 1).

Since the interferogram depends on the optical properties of the polymer, the thickness of the film, and the gases, different parameters have been used to simulate optimal thicknesses of the layers and ratios of refractive indices. In fig. 5 the result is given for 2 types of polymers, a polysiloxane and a polystrol film [13]. To obtain a good interference pattern it is necessary to have some difference in the refractive indices (for polysiloxane n-1,4 and polystrol n-1,5) as well as a difference in the physical thicknesses. These optimization procedures are necessary, otherwise experimental variation of the film thicknesses turned out to be not successful.

gas	polymer 1	polymer 2
n-pentane	15	9
n-hexane	33	26
n-heptane	100	100
n-octane	182	294
cy clohexane	65	56
dichloro me thane	18	13
trichloromethane	4T	39
tetrachloromethane	TT	69
benzene	96	51
toluene	203	158
m-xylene	502	521

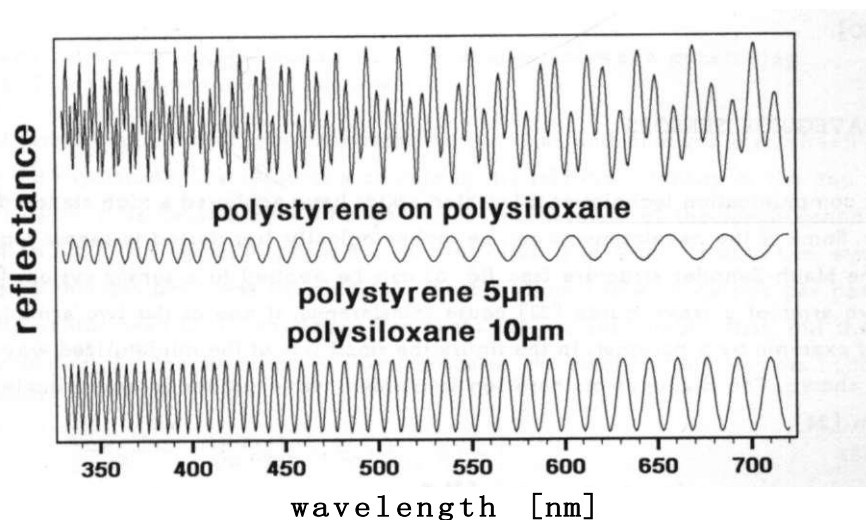table 1: Change of optical pathlength in %, reference is n-heptane taken to 100 %.

fig. 5: Resulting interference spectrum for multi-reflection at a bi-layer interface.

MULTICOMPONENT ANALYSIS AND PATTERN RECOGNITION

In principle, spectral measurement allows either to implant more than one indicator dye in the sensor head or to construct multi-layers which show the interferences discussed before. Multilinear regression has been used many times in multi-component analysis [14]. It requires all the components present in the sensor head to be known by calibration spectra. Therefore cross-interferences by unexpected components cannot be avoided in analytics.

For this reason, principles of pattern recognition have been applied to this type of multi-component analysis. Principle component analysis CPCA) [15] allows to verify

the expected number of components taking part in the analysis. But, the calculated principle components lack physical properties. Therefore, in many cases factor analysis [16] is used, which includes a target transformation [IT]. The principle components are "rotated". This mathematical procedure results new values which represent the concentrations of the components, too. In all these cases, pattern recognition methods have to be combined with the method of multi-component analysis.

Another approach is given by the partial least squares (PLS) method. The differences between PCA and PLS are perfectly reviewed in [18]. All these approaches - even the multi-calibration approach of partial least squares - in principle require linear dependence between the parameters. Now, it is known that in the case of sensors this linearity cannot be expected always. For this reason, a specific type of Kalman filter [19], the so-called adaptive Kalman filter, is going to be tried in the case of sensor arrays [20].

WAVEGUIDE SENSORS

In communication techniques integrated optics have achieved a high standard recently. Some of the developments can be technologically transferred to sensor techniques. The Mach-Zehnder structure (see fig. 6) can be applied to a sensor system [21]. The two arms of a wave guide [22] cause interference, if one of the two arms is coated for example by a polymer. In the figure the small size of the miniaturized wave guides is shown. The diameter of these ion implanted wave guides is approximately 5 - 8 ttm [24].

(b)

substrate   surface aratieguide
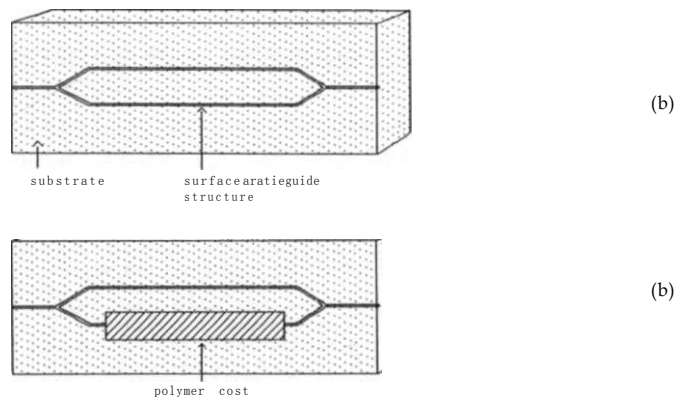   structure

(b)

polymer cost

fig. 6: Schematic representation of a wave guide: (a) structure (b) polymer coated

As Fig. 7 shows, the evanescent wave propagating in the wave guide obtains information about the substrate as well as the superstrate. Different velocity of the propagating waves in the two arms can cause an extinction of the electromagnetic waves. By these means information about the superstrate is obtained.
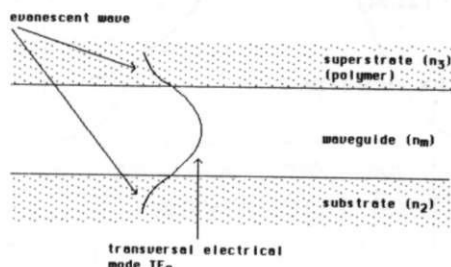

fig. 7: Mach-Zehnder integrated optic chip [23]: evanescent wave penetrating substrate and superstrate (side view).

Using this system as a sensor, gas penetrates the polymer and changes the refractive index of the superstrate. The result is a change in the relative intensity at the end of the waveguide. It is caused by a change in the interference of the Mach-Zehnder structure. In fig. 8 two negative peaks are demonstrated. This signal is obtained, even though only one gas peak was injected into the continuous flow of carrier gas passing by the sensor head [23]. These negative peaks are not reasonable, first. But they can be explained by the equations for the change of the electric field vectors in the wave guide:

$$\frac{\delta^2 E_{oy}(x')}{\delta x'^2} - V_o^2 (a_{TE} + b_o)\, E_{oy}(x') = 0 \tag{5}$$

$$\frac{\delta^2 E_{oy}(x')}{\delta x'^2} + V_o^2 \left[f(x') - b_o \right] E_{oy}(x') = 0 \tag{6}$$

$V_o = b_x k_o \sqrt{(n_m^2 - n_2^2)}$ standarized waveguide depth

$b_o = \dfrac{(n_{eff}^2 - n_2^2)}{(n_m^2 - n_2^2)}$ standarized mode refractive index

$a_{TE} = \dfrac{(n_2^2 - n_3^2)}{(n_m^2 - n_2^2)}$ asymmetrical factor

$f(x') = e^{x'^2}$ refractive index profile

n_m: refractive index of the waveguide E_{oy}:   field of the TE-mode
n_2:   refractive index of the substrate k_o: wave vector ($2\pi/\lambda_o$)
n_3:   refractive index of the superstrate λ_o: wavelength
n_{eff}:   refractive index of the TE-mode b_x: waveguide depth
x': x/b_x, on the waveguide depth standarized coordinate

These equations describe the continuity conditions at the interfaces between super-

strate/waveguide/substrate. Therefore, a closed solution is necessary. This is impossible, because of the second equation. For this reason, one can simulate dependencies of the signal on the refractive index profile, the length of the arm covered with polymer, the wavelength, and the refractive index of the superstrate. The result of these calculations is given in fig. 9 [22,24].
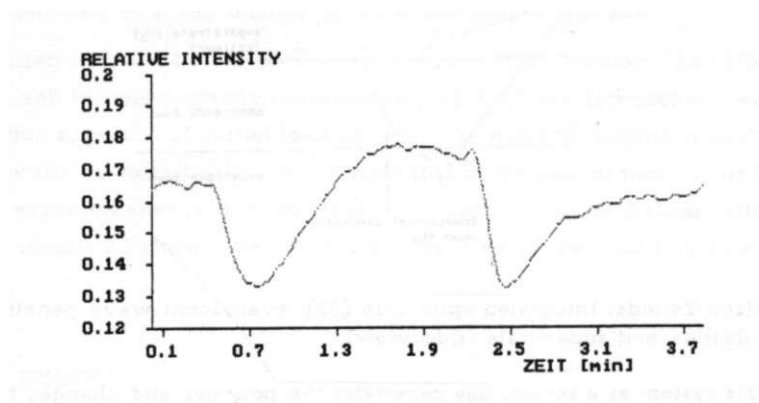

fig. 8: a small amount of toluene is injected in a carrier gas (one peak), observed are two peaks in a measurement inensity signal vs. flow time

In fig. 9a the calculation was done for a fixed length of the polymer, and the refractive index of the superstrate for evaluation in wavelength. In fig. 9b the wavelength was taken fixed, whereas the refractive index of the superstrate was varied. In fig. 8c the length of the polymer film was varied for a fixed refractive index of the superstrate for some wavelengths. Taking fig. 9b the experimental result can be understood. The gas intruding the polymer will change the refractive index. In this case the refractive index is increased (refractive index of the gas is higher than the polymer). In fig. 9b one starts at the start point and declines the refractive index curve. For increasing concentration a reduction in intensity is the consequence according to the simulated curve given in the figure. Further increase in gas concentration beyond the minimum in the curve results a higher signal until the highest gas concentration is reached. Then, the gas concentration becomes smaller. For this reason, the refractive index increases back again. The signal "follows" the simulated curve back to the start point. This explains the second minimum in the experimental curve (fig. 8).

CONCLUSION

The given examples were used to demonstrate that computers are not only meaningful in sensor applications, but will even allow to understand material-analyte interactions by use of sophisticated computerized measurement set-ups. Furthermore, simu-
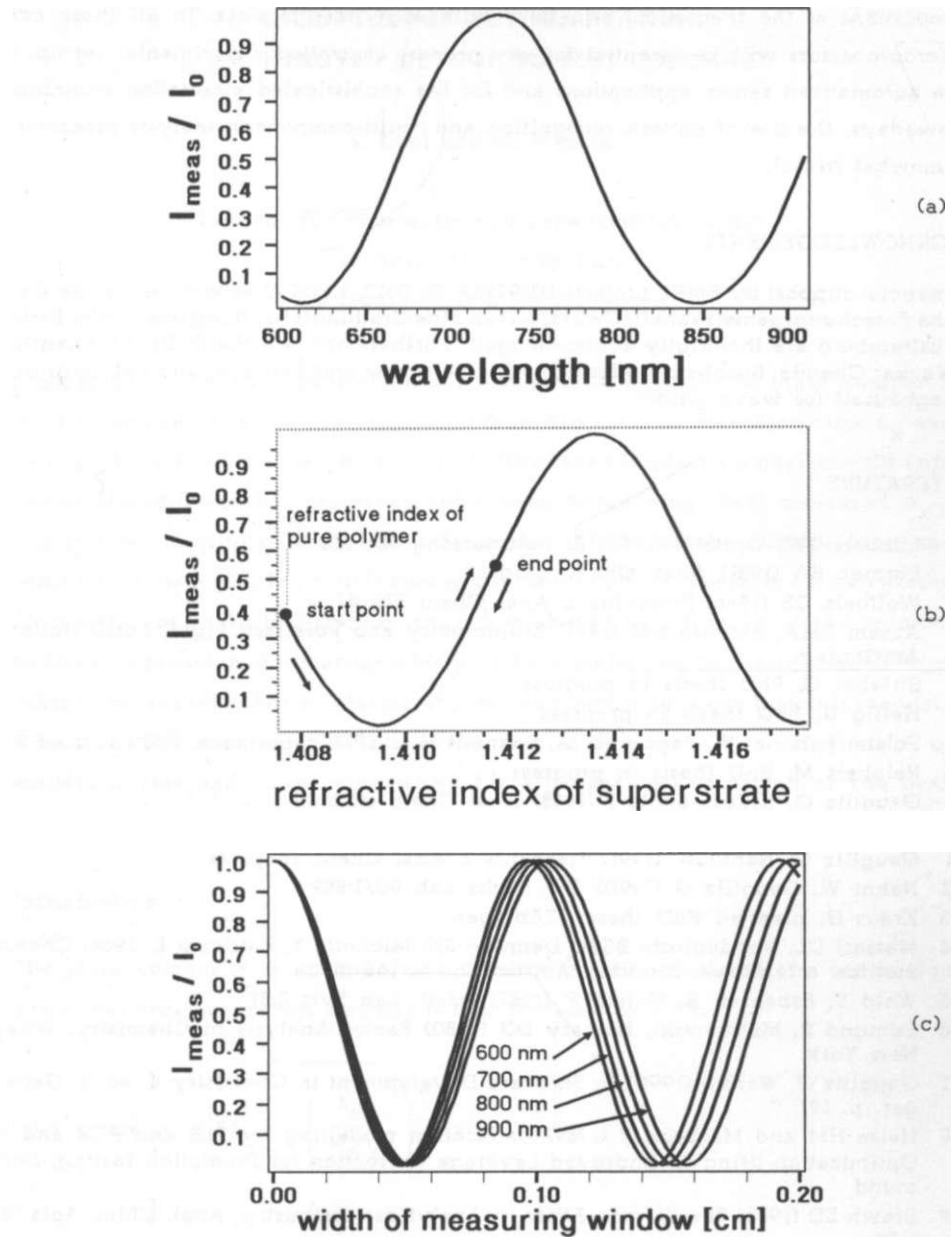
fig. 9: Runge-Kutta-Simulation for changes in wavelength (a), refractive index (b), and measuring window (c).

lations can explain unexpected experimental curves by graphical comparison of the

simulations of the theoretical equations with experimental data. In all these cases microprocessors will be essential for any process controlled experimental set-up, for the automatized sensor applications and for the sophisticated evaluation techniques. Nowadays, the use of pattern recognition and multi-component analysis programs is somewhat trivial.

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