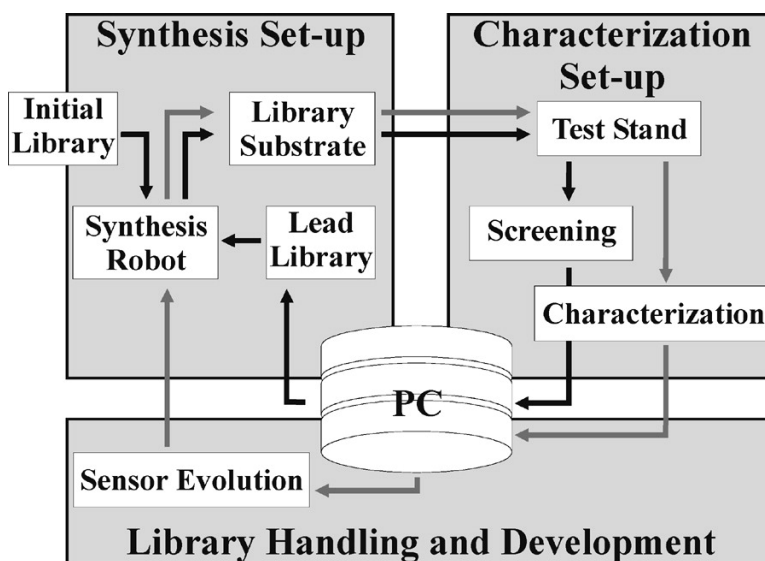Article

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A Combinatorial Approach for Development of Materials for Optical Sensing of Gases

Athanasios Apostolidis,[†] Ingo Klimant,[‡] Damian Andrzejewski,[†] and
Otto S. Wolfbeis*,[†]

*Chemo- and Biosensors, Institute of Analytical Chemistry, University of Regensburg,
D-93040 Regensburg, Germany, and Micro- and Radiochemistry, Institute of Analytical Chemistry,
Technical University of Graz, A-8010 Graz, Austria*

We present a combinatorial approach for development of materials for use in optical gas sensors, with oxygen being used as an exemplary target gas. Combinatorial chemistry is shown to be a promising tool for speeding up the search for new sensor materials. The method is based on the use of various polymers, solvents, indicators, plasticizers, and other additives. Solutions of the respective materials are prepared in appropriate organic solvents, and a robotic station is programmed to mix the components. Spots of the sensing materials are deposited in the wells of glass substrates resembling microtiterplates. After drying off the solvent, the sensor spots are automatically analyzed in a test stand, where they are exposed to a carrier gas containing oxygen in various concentrations. Changes in the decay time of fluorescence of the indicator probes are measured and used (along with sensor response time) as a main criterion for sensor assessment. It is shown that the combinatorial approach can reduce the time and effort needed to establish libraries of sensor materials by a factor of at least 1000. We describe in detail the device for preparation of sensor libraries and for testing the respective materials. The potential of the system is demonstrated for the characterization of optical oxygen sensors.

Introduction

Combinatorial chemistry (CC) is one of the most impressive technologies developed in the last several years. Its application meanwhile has extended far beyond peptide chemistry and is used now in a manifold of areas including, more recently, material sciences. CC and high-throughput methods for screening have found numerous applications, for examples in life sciences or catalysis.[1−4] Another research topic is the development of molecular receptors for chemosensors.[5,6] The optimization of materials compositions, such as for homogeneous or heterogeneous catalysts, for nanoscale materials, and for the optimization of process parameters of materials fabrication are examples of research that involve high-throughput approaches.[7−10]

Since the development of sensor materials is still very often a kind of empirical ("trial and error") science, the automation of material blending and calibration is key to the speed-up of production of optimized materials. In addition, it can be a tool to a better comprehension of sensor properties. Along with new techniques for synthesis (or material formulation, as shown here), instrumentation for making material libraries (including solid materials) has been continuously improved in the past few years. Systems for powder-, paste-, or liquid-handling systems are commercially

available now, as are automated reaction-handling systems for solid-phase synthesis.

Conventional serial sensor development requires intensive research in planning of possible sensor compositions. Assuming a typical optical gas sensor to be composed of a supporting matrix and several target-sensitive components and fine-tuning additives, the number of possible combinations rapidly rises to dimensions that hardly can be handled in conventional laboratories. By using 10 different species of each component in a ternary mixture, the number of sensors to be manufactured and tested is 1000. Varying the concentration of sensitive components and additives 10 times each for the validation of the optimal sensor composition and producing at least three samples per sensor for statistically significant analysis spread up the matrix to 3×10^5 different sensor materials. Typically, the realization of the preparation and the characterization test of each sensor requires 2−4 h in total. Hence, the analysis of such a data matrix would involve up to 12×10^5 man hours of work.

Automation is the key to overcome the bottlenecks of conventional sensor development. CC results in speed-up and scale-down of sensor preparation and characterization. Preparing 60 samples at a time along with the parallel or high-throughput characterization of sensor samples cuts the time required for the realization of 12×10^5 sensors by a factor of 60^2. As a result, less than 3 months is required to realize the same data matrix. Along with the automated production of experimental data, tools are needed for handling those.

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* To whom correspondence should be addressed. E-mail: otto.wolfbeis@chemie.uni-regensburg.de.
† University of Regensburg.
‡ Technical University of Graz.

Table 1. List of Polymers, Solvents, Plasticizers and Indicators Used[a]

Polymers	Solvents
ethyl cellulose (ethoxy content 46%) (EC46)	toluene/ethanol (80/20) v/v
ethyl cellulose (ethoxy content 49%) (EC49)	toluene/ethanol (80/20) v/v
poly(tetrafluoroethylene-*co*-vinylidenfluoride-*co*-propylene) (PTFE-coVP)	tetrahydrofuran
poly(styrene-*co*-acrylonitrile) (PSAN)	chloroform
cellulose acetate (CAc)	chloroform
poly(4-vinyl phenol) (PVPh)	tetrahydrofuran
poly(vinyl methyl ketone) (PVMK)	toluene/ethanol (80/20) v/v
polysulfone (PSu)	chloroform
poly(vinyl chloride-*co*-isobutyl vinyl ether) (PVCE)	toluene/ethanol (80/20) v/v
poly{[octahydro-5-(methoxycarbonyl)-5-methyl- 4,7-methano-1*H*-indene-1,3-diyl]-1,2-ethanediyl} (POMMIE)	toluene/ethanol (80/20) v/v
poly(bisphenol A carbonate) (PC)	chloroform
poly(4-*tert*-butylstyrene) (PTBS)	toluene/ethanol (80/20) v/v
poly(acrylonitrile) (PAN)	DMF
poly(vinyl chloride) (PVC)	tetrahydrofuran
polystyrene (PS)	toluene/ethanol (80/20) v/v
poly(methyl methacrylate) (PMMA)	chloroform

Plasticizers	Indicators
tributyl phosphate (TBP)	$Ru(4,4'$-diphenylbipyridyl$)_3TMS_2$
tris(2-ethylhexyl) phosphate (TOP)	$Ru(4,7$-diphenylphenanthroline$)_3TMS_2$
2-(octyloxy)benzonitrile (OBN)	Pt(II) tetrakis(pentafluorophenyl)porphyrin
nitrophenyl-octyl ether (NPOE)	Pd(II) tetrakis(pentafluorophenyl)porphyrin

[a] The total matrix tested consisted of all conceivable combinations among polymers, plasticizers, and indicators in the list. Plasticizers were employed in concentrations of 0, 10, 33, and 50% (w/w), in the sample cocktails. All indicators were employed in a concentration of 0.5% (w/w) in the cocktails.

Unlike in conventional methods, the main effort in this type of CC is in (a) the planning and design of blending routines, (b) the design and automation of the test stand, and (c) fast evaluation of sensor properties. Depending on the target molecule and the analytical method, both devices and methods need to be adjusted. We present here a scheme for the combinatorial formulation and high-throughput characterization of materials for an optical gas sensor. Specifically, the approach is applied to the development of sensor materials for oxygen since optical (fiber) oxygen sensors display excellent performance (when compared to the well-established oxygen electrodes) and have successfully been introduced into (commercial) sensors for blood oxygen analysis,[12−15] to bacterial detection,[16] in open-heart surgery,[13,17] in invasive fiber-optic catheters,[12,18] and in bioreactor monitoring.[19] Numerous other applications are conceivable. For example, Dickinson and Walt[20] have shown that a substantial sensor diversity can be generated by combinatorial polymer synthesis and testing the resulting materials for sensitivity to organic vapors. We also present a study on the effect of the structure and content of plasticizer in various polymer matrixes on the response characteristics of the optical sensing films. It should be noted, though, that the purpose of the contribution is to apply new combinatorial methodology to advance the screening process (rather than to identify specifically suited materials for oxygen sensing). In future work, we intend to show that the approach is applicable to the development of improved materials for sensing gases and ions.

Experimental Section

Chemicals. The following polymers were employed (also see Table 1): ethyl cellulose with an ethoxy content of 46% (referred to as EC46) and 49% (EC49), poly(tetrafluoroethylene-*co*-vinylidene-*co*-propylene) (PTFE-coVP), poly-{[octahydro-5-(methoxycarbonyl)-5-methyl-4,7-methano-1*H*-indene-1,3-diyl]-1,2-ethanediyl} (Product No. A46710; referred to as POMMIE), poly(styrene-*co*-acrylonitrile) (PSAN), cellulose acetate (CAc), poly(4-vinylphenol) (PVPh), poly-(vinyl methyl ketone) (PVMK), polysulfone (PSu), poly-(vinyl chloride-*co*-isobutyl-vinyl ether) (PVCE), poly-(bisphenol A carbonate) (PC), poly(acrylonitrile) (PAN), poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA), poly(4-*tert*-butylstyrene) (PTBS), and polystyrene (PS). All were purchased from Aldrich (www.sigmaaldrich.com). The plasticizers tributyl phosphate (TBP), tris(2-ethylhexyl)phosphate (TOP), 2-(octyloxy)benzonitrile (OBN), and nitrophenyloctyl ether (NPOE) were purchased from Fluka (www.sigmaaldrich.com).

The fluorescent probes $Ru(4,4'$-diphenylbipyridyl$)_3TMS_2$ [referred to as Ru(diphbipy)$_3$] and $Ru(4,7$-diphenylphenanthroline$)_3TMS_2$ [referred to as Ru(dpp)$_3$] were purchased from Chromeon (www.chromeon.com). The complexes of Pd(II) and Pt(II) with 5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrin were from Porphyrin Systems (www.porphyrinsystems.de). Ethanol, toluene, chloroform, and tetrahydrofuran were purchased from Merck. Oxygen, synthetic air (20.9% v/v oxygen in nitrogen), and nitrogen were purchased from Linde GmbH, Germany (www.linde.de). All chemicals were of analytical grade and were used without further purification. Gas blends of defined oxygen concentration were produced by using computer controlled mass flow controllers (type 1179A; from MKS Instruments, www.mksinst.com).

Instrumentation for Material Blending. The sensor materials were manufactured with a computer-controlled

Table 2. Dynamic Quenching of the Fluorescence of Ru(dpp) Expressed as the Reduction in Decay Time $[(\tau_0/\tau) - 1]$ at 100% Air Saturation in Various Polymers with Fractions of Plasticizer Ranging from 10 to 50% (w/w)

polymer	plasticizer	quenching at 20.9% oxygen in nitrogen			
		0% plasticizer	10% plasticizer	33% plasticizer	50% plasticizer
EC46	TBP	1.04	1.19	1.66	2.33
EC46	TOP	1.04	1.08	1.46	1.92
EC46	OBN	1.04	0.82	1.34	2.03
EC46	NPOE	1.04	0.82	1.25	1.85
EC49	TBP	1.14	1.24	1.63	2.51
EC49	TOP	1.14	1.18	1.56	2.03
EC49	OBN	1.14	0.93	1.49	2.17
EC49	NPOE	1.14	0.94	1.38	2.04
PTFE-coVP	TBP	0.79	1.52	3.32	4.46
PTFE-coVP	TOP	0.79	1.58	2.00	1.53
PTFE-coVP	OBN	0.79	0.71	1.15	1.45
PTFE-coVP	NPOE	0.79	0.59	0.99	1.20
POMMIE	TBP	0.41	0.41	0.61	0.73
POMMIE	TOP	0.41	0.35	0.52	0.86
POMMIE	OBN	0.41	0.24	0.51	1.15
POMMIE	NPOE	0.41	0.25	0.41	1.02
PS	TBP	0.34	0.29	0.31	0.91
PS	TOP	0.34	0.27	0.42	0.57
PS	OBN	0.34	0.21	0.57	1.20
PS	NPOE	0.34	0.22	0.53	1.09

liquid-handling robot (MicroLab S, from Hamilton Bonaduz AG; www.hamiltongmbh.de)) by mixing of stock solutions of polymers, plasticizers, and indicator dyes. Protocols for the mixing steps were developed to realize the possible combinations of components for the sensor materials. The volumes of the respective solution of the component for the sample materials were mixed in sample vials placed on one side of the working area of the robot. After preparation of the cocktails, glass substrates placed on the free side of the working area were loaded with the sample solutions, and the solvents were evaporated. The supporting glass substrates were prepared by etching wells (6 mm diameter) into glass slides ($65 \times 105 \times 1.1$ mm^3) made from borosilicate glass using hydrogen fluoride and an etching mask.

Device for Material Characterization. The apparatus used for the calibration of the sensor materials was composed of the following modules: (1) a gas flow cell, (2) a gas mixing device with mass flow controllers, (3) an $x-y$ table for positioning of the detector head, (4) a detection unit with a dual branch glass fiber bundle as a light guide for illumination and luminescence detection, (5) a combination of a photomultiplier tube (PMT, Hamamatsu Photonics; www.hamamatsu.de) and a lock-in amplifier (DSP SR830, from Stanford Research Systems; www.srsys.com) for the acquisition of intensity and phase shift of sensor luminescence, and (6) a PC for synchronization and control of the modules. Blue LEDs (Product No. NSPB500S, Nichia) and green LEDs (Product No. NSPG500S, Nichia; www.nichia.com) with peak wavelengths of 470 and 530 nm, respectively, were used for fluorescence excitation of the sensor materials. The ruthenium dyes were characterized using the blue LED with a BG-12 as an excitation filter and an OG-570 as emission filter. The modulation frequencies were 90 kHz for Ru(diphbipy)$_3$ and 45 kHz for Ru(dpp)$_3$. For the Pt(II) complex, the green LED with an FITC excitation filter and an RG-630 emission filter was used. The LED was modulated at 5 kHz. Figure 2 shows a schematic illustration of the device.
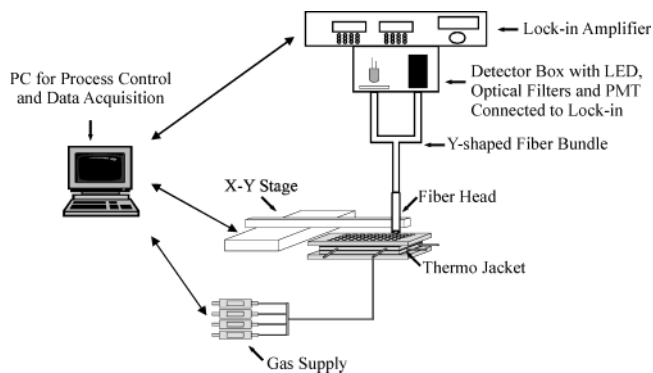
Figure 1. Schematic view of the test rig with gas cell, $x-y$ translation stage (with fluorescence detector head), lock-in amplifier, light source, and gas supply. The PC controls and synchronizes the modules and stores the data acquired with the lock-in amplifier.
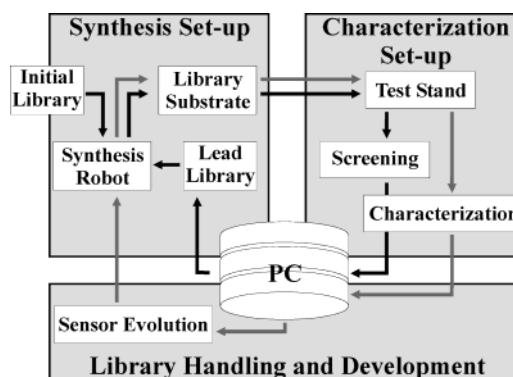
Figure 2. Visualization of the single-process steps in the combinatorial development of new sensor materials.

Preparation of Oxygen Sensor Material Libraries. Oxygen sensor materials are typically composed of a polymer, a fluorescent (quenchable) probe, and (sometimes) a plasticizer. Oxygen acts as a quencher of fluorescence, and the change in the optical signal serves as the analytical information. The quenching efficiency strongly depends on the type of polymer used[11,22,23] and, thus, can be fine-tuned by proper choice of the polymer matrix.

Polymer stock solutions of defined concentration were prepared by dissolving the polymer in a solvent (see Table 1). Indicator stock solutions were prepared by dissolving 20 mg of the respective indicator in 5 mL tetrahydrofurane. The stock solutions of polymer, indicator dye, and in some cases plasticizer were mixed by the robot to create the sample cocktails. A blending algorithm developed with the MicroLab S sampler software (MSS) controlled all steps of the production of the cocktails. The composition of the sensor material was predetermined by an Excel sheet containing the concentrations of the stock solutions of the components. The matrix of ingredients for the preparation of sensing materials is illustrated in Table 1. It also includes the solvents used for a very practical reason: most polymers require rather specific solvents in order to warrant adequate processing of the material "cocktails" (dissolved polymers/indicators/plasticizers) with the liquid-handling robot. If inadequate solvents are chosen, components may precipitate. Thus, customization of the robot and the selection of chemicals is substantial.

Polymers were chosen according to (a) commercial availability, (b) gas permeability (most data available from handbooks), (c) stability, and (d) solubility. Plasticizers were chosen according to compatibility, and indicators were selected according to (a) compatibility with LED- and diode laser light sources, (b) availability/accessibility, and (c) sensitivity to oxygen.

The standard sample composition was fixed to 15 mg of supporting polymer and an indicator concentration of 0.5% (w/w) in this worksheet. The concentration of the plasticizer was varied from 0 to 50% (w/w) of polymer matrix. The volumes needed to create this composition were calculated by the blending algorithm from the data given in an Excel sheet.

After preparation, the cocktails were transferred to the glass substrate with the MicroLabS robot (according to a transfer protocol written with the MSS software), and the solvent was then evaporated. The software-controlled production of the sensor material libraries provides an indexing of the sample libraries containing the composition of the respective sensor material on a substrate.

Material Characterization. Optical sensors typically respond to the analyte by a change in either the intensity of light; its polarization; or in the case of fluorescence, by a change in decay time of the efficiency of energy transfer (FRET). In the case of oxygen sensors, decay time is the preferred parameter,[21] since it is intrinsically referenced.

The glass substrates with the sensor materials in the wells were placed in a sealed chamber and exposed to varying oxygen concentrations by blending 20.9% (v/v) oxygen in nitrogen with nitrogen of 99.999% purity. The appropriate ratios were adjusted via the mass flow controllers. Luminescence intensity and phase shifts (ϕ) between excitation and emission phases were acquired with the lock-in amplifier by positioning the fiber bundle over the respective sensor spot. In theory, the quenching of a luminophor distributed homogeneously in the polymer matrix fits a simple Stern—Volmer equation, that is,

$$\frac{\tau_0}{\tau} = 1 + K_{SV}pO_2 \tag{1}$$

where τ_0 and τ are the decay times of the luminophor in nitrogen and in the presence of oxygen at a partial pressure, pO_2, in millibars. K_{SV} is the Stern—Volmer quenching constant. The ratio of the decay times was calculated from the equation

$$\tau = \frac{\tan \Phi}{2\pi f_{mod}} \tag{2}$$

where f_{mod} is the modulation frequency of the LED, and ϕ is the phase shift in the respective atmosphere. All measurements were performed at 22 °C.

Results

Strategy of the Combinatorial Approach. The combinatorial approach to the development of new sensor materials can be divided into (a) library design, (b) combinatorial mixing, (c) high-throughput characterization of the sensor materials produced, and (d) database-supported library handling and evolution. Sophisticated instrumentation is needed and, in particular, involves units to control and synchronize all process steps. The schematic view in Figure 2 displays the steps during the development of new sensor materials by combinatorial blending and high-throughput characterization (HTC) as well as the relationship of the components in this approach.

Library Design. The combination of polymers, plasticizers and indicator dyes in various ratios defines a set of sensor materials (the library). In practice, the library has to be split into sublibraries that can be handled with the instrumentation used for the calibration of the sensor materials (the "initial library"). The characterization setup is designed for handling 60 sensor spots that can be placed on the glass substrates used. For statistically significant analysis, at least three identical sensor spots have to be prepared. As a result, 20 different sensor materials can be calibrated in one cycle. The luminescence intensities and the phase shifts between excitation and emission phases of luminescent dyes are acquired as the "sensor information" using the device described before. Optical filters adjusted to the emission wavelengths of the dyes are used to separate the luminescence detected with the PMT from background fluorescence. The optical filters, the modulation frequency of the LED and the LED have to be changed each time when changing the luminescent indicator dye. To minimize the total number of exchanges, the sensor materials are arranged on the glass substrates as a series of sensor materials with the identical indicator dye to be tested.

Combinatorial Blending. To warrant a minimum of technical instrumentation for automated mixing of sensor materials, it is necessary to adjust the method of sensor preparation. This is associated with the physical and chemical properties of the sensor components, for example, the solubility of polymers and additives in a solvent. Under the stipulation that all components are soluble in an organic solvent, it is possible to prepare sample cocktails by mixing solutions of the ingredients using a liquid-handling robot.

In practice, it turned out that not only the sensor chemistry has to be adjusted, but also the technical equipment has to be tested for their chemical resistance against the organic solvents used. In particular, all solvent supply pipes have to be manufactured from PTFE or analogous materials when using tetrahydrofuran or other aggressive organic liquids as working solvent. Tubings made of PVC, for example, are inadequate in this case.

The device used for the preparation of material mixtures ("cocktails") is the tool to realize the combinatorial libraries. Stock solutions of the components are placed on the racks on the work space of the robot. From there they are dispensed to a rack containing flasks for the sensor cocktails. The composition of the sensor materials is given by an external source, that is, an Excel worksheet. Algorithms are developed to process these sheets with the dispenser operating software. The volumes needed of each component are defined by the worksheet and are aspirated from the stock solutions and dispensed to the sample flasks with subsequent mixing. The resulting sample cocktails are transferred to the wells of the glass substrates, and the solvent is evaporated. The sample library thus obtained is placed in the characterization device, and the sensors are tested for response to oxygen.

High-Throughput Characterization. The test stand for characterizing the sensor materials consists of a gas mixing device to provide atmospheres of defined oxygen concentration, a test chamber where the sensor materials produced are exposed to the gas and a unit for the detection of the fluorescence signal. The glass substrates used were designed to match the size of the test chamber. The size and the position of the etched wells on the glass substrate were in the same shape as in the case of widely used microtiterplates in order to be able to exchange the gas chamber for a microtiterplate format for measurements of sensors in liquid media.

The detection unit is configurable to the method used for signal detection. In the case of oxygen sensors, the fluorescence properties of the sensor materials are detected. The sensor spots are illuminated with an LED, and luminescence is detected by photomultiplier tubes or photodiodes. For absorbance measurements, the absorbance of the samples is detected via scanning spectrometers or compact spectrometers (so-called multichannel analyzers), covering the visible and near-infrared region of the spectrum. The detector is moved to each sample spot to measure the optical properties with two-step motors arranged rectangularly on an x–y translation stage.

Library Handling. The preliminary screening of the libraries delivers a set of data describing the change of the optical properties of the sensors after changing the gas atmosphere to which the sensor spot is exposed. These data are also used for the characterization of the materials. Thereafter, a first selection of hits is carried out. These hits are combined into so-called lead libraries that subsequently are analyzed in more detail to give a second set of data. The materials with the most promising response are extracted and undergo an evolutionary process in which the sample composition is fine-tuned in order to obtain spots that display the best performance. This procedure is repeated several
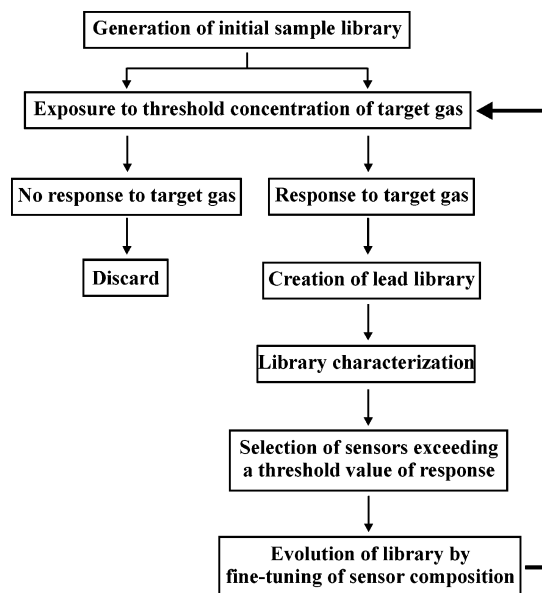

Figure 3. Flowchart of sensor material development by combinatorial blending and of characterization of optical sensor materials.

times until a set of optimal new sensor materials can be extracted. Figure 3 shows a flowchart that outlines the strategy. The process leads to various materials (composed of polymer and indicator) that are referred to as a selection of hits combined to a lead library. The introduction of plasticizers is the next step in order to fine-tune the sensory properties of the materials.

The combinatorial approach to material formulation and characterization was successfully applied to the preparation and the characterization of oxygen sensors. The method enabled the fast production of 64 initial sensor materials from a matrix of four oxygen-sensitive indicators and 16 polymer matrixes. The library was characterized by recording the phase shift of the dye luminescence incorporated in nonplasticized polymer matrixes for all polymers used with varying the oxygen partial pressure from 0 to 100% air saturation. By using these data, we have established Stern–Volmer plots for each dye–polymer matrix, as illustrated in Figure 4, for a selection of polymers with Ru-(dpp)$_3$ as the indicator dye. The reproducibility, expressed as the standard deviations of τ_0/τ (for $n = 6$) of Ru(dpp) in EC46 was found to be 0.60% at 10 mbar, 0.62% at 20 mbar, 0.62% at 51 mbar, 0.64% at 102 mbar, and 0.64% at 204 mbar.

Following the initial study, two indicators, six polymers and four plasticizers were identified to build up a second library, then the plasticizer concentration was varied in steps of 0, 10, 33 to 50% (w/w). Again, the combinatorial approach enabled a substantial speed-up of production and characterization of sensor materials. A library of $6 \times 2 \times 4 \times 4 = 192$ compositions was produced and characterized within 1 week.

For the characterization of the sensor materials, the phase shifts between excitation and emission of the dye luminescence was recorded when varying the oxygen partial pressure from 0 to 100% air saturation. Stern–Volmer slopes (K_{sv} in eq 1) were calculated to characterize the materials. A comparison of the sensor materials with respect to matrix
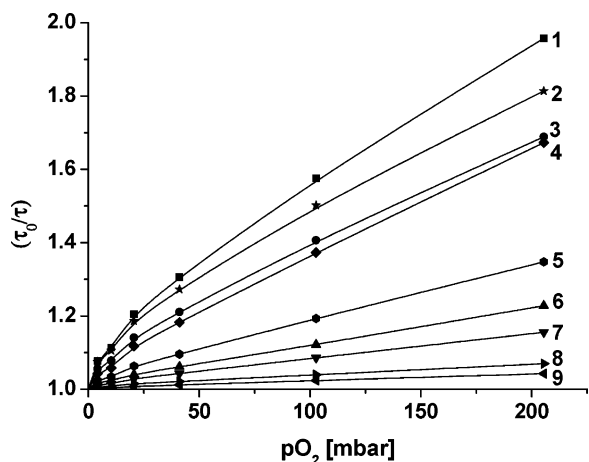
Figure 4. Stern−Volmer plots of (τ_0/τ) versus pO_2 for the oxygen probe Ru(dpp)$_3$ dissolved in polymers EC46 (1), PTBS (2), EC49 (3), CAc (4), POMMIE (5), PTFE−coVP (6), PSAN (7), PVMK (8), and PVPh (9).
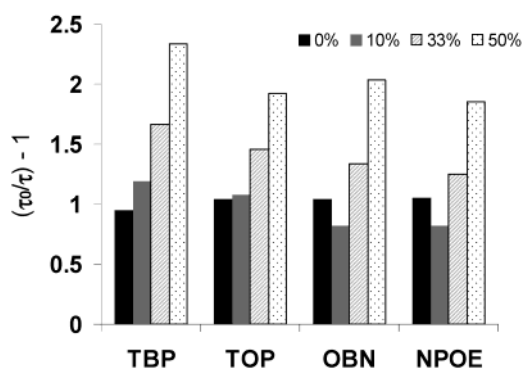

Figure 5. Effect of type and concentration of plasticizer on the sensitivity of fluorescent oxygen-sensing materials using EC46 as the supporting matrix and Ru(dpp)$_3$ as the quenchable oxygen probe.

composition is possible by comparing the average slopes of the calibration plots. For this purpose, the materials can be discriminated by dividing the library into groups of samples containing identical indicator dyes as a first differentiating criterion. The materials are then differentiated in more detail via the type of polymer and the type of plasticizer. The two main criteria for sensor assessment are quenchability (expressed by K_{sv}) and response time.

It is found that the initial slope of the sensor response can be widely tuned by introduction of plasticizers into the sensor material. The sensitivity of the system increases with increasing fractions of plasticizer. This can be attributed to an increase in the permeability of oxygen in the matrix, as shown in Figure 5. Plasticizing with 10% w/w OBN and NPOE causes an initial decrease of sensitivity with respect to nonplasticized matrixes, but on increasing the fraction of plasticizer to 33% (w/w), the sensitivity of nonplasticized sensing films is exceeded again.

Discussion

We show that the combinatorial approach to production and characterization of optical oxygen sensors can considerably speed up the development of sensor materials. The test stand used can be easily adjusted to other target gases by changing the sensor chemistry. The target gases can be

selected from all those causing a change in the respective optical properties of the sensor material. The system may be modified in order to test liquid systems. The gas cell used in this work was replaced by a holder of microtiterplates, and this enabled the study of solution parameters, such as dissolved oxygen, pH, or heavy metals. In future work, we want to employ a CCD camera in order to image the library, thereby further cutting down the scanning time and reducing the number of moving parts.

It was not the aim of this study to identify new materials of a specific kind for purposes such as low-level sensing of oxygen. Rather, it was intended (a) to prepare a number of materials, (b) to have available a wide variety of materials from which those that are adequate for a certain application may be picked, and (c) to learn more about relationships of the effect of polymers on the general properties of optical sensor materials. Very recently, Amao[24] reviewed polymers and probes for use in oxygen sensors, and this article clearly shows that we still lack a basic understanding of why certain materials are more useful (or so much more sensitive to oxygen)[25] than others. Combinatorial approaches clearly offer an alternative to the cumbersome search for new materials on the basis of theoretical predictions, which so often is hampered by practical limitations, such as poor compatibility of solvents, polymers, indicator dyes, and plasticizers, but also by solubility. Thus, the approach presented here is of general significance for developing gassensitive materials and will facilitate future strategies for blending and characterizing materials so as to overcome the present bottlenecks in conventional sensor material development.

Note Added after ASAP Posting. In Table 2, the percentage of oxygen in nitrogen was corrected to 20.9%. The corrected version of the paper was posted on March 2, 2004.

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