

## A Study of Optical Chemosensor Materials

Khlebunov A., Ionov D., Aristarkhov V., Sazhnikov V., Alfimov M.  
Photochemistry Center, Russian Academy of Sciences,  
ul. Novatorov 7a, Moscow 119421, Russia

An experimental setup for determination of optical and functional properties of optical sensor materials, particularly materials based on fluorescent micro- and nanoparticles is described. The system allows one to prepare multicomponent vapor mixtures, measure the fluorescence and reflection spectra and images of sensor materials with time resolution of several milliseconds. The system can be used for training electronic noses based on optical sensor materials. Examples of studying sensor materials and sensor arrays are presented.

### Introduction

The field of optical chemical sensors (OCS) has been a growing research area over the last three decades. Recent developments in this field have been driven by such factors as the availability of low-cost, miniature optoelectronic light sources and detectors, the need for multianalyte array-based sensors (particularly in the area of biosensing) (Donagh et al, 2008; Borisov and Wolfbeis, 2008 ). Each sensor system contains three main elements: a sensor layer (sensor material), a transduction platform and signal-processing electronics.

One of perspective transduction platforms is an array of sensor elements each of them represents an ensemble of fluorescent functional micro- or nanoparticles (Tam et al., 2005, Wu et al., 2008). One of advantages of such platform is an opportunity of integration a light source, a photodetector and an energy source in one chip. The sensor material on the base of fluorescent particles made by immobilizing a fluorescence dye on the surface of a micro- or nanoparticle (e.g. polymer, ceramic, metal) has several advantages in comparison with common sensor materials (e.g. dye doped polymer film). Application of such materials in sensor systems significantly improves performance of the systems. Development of optical sensor materials based on micro and nanoparticles with dyes immobilized on their surface is promising for further optical chemical sensors and electronic nose systems progress (Dickinson et al., 1996). There are three main advantages of the sensor materials: a wide range of materials can be created by combining different dyes, particles and methods of immobilization, a chemical modification of the indicator dye and the surface of the particle permit functional characteristics of material to be tailored for specific analyte or a group of analytes (Pearce and Sanchez-Montanes, 2003), immobilization of indicator dyes on the surface of the particles significantly decreases response time and relaxation time of materials, because analytes does not need to diffuse into the volume of a material.

A response of a sensor material to an analyte is the result of complex interactions in a system analyte/indicator/polymer (Plotnikov et al., 2007). To study such materials is

necessary to control greater amount of experimental parameters. Thus, standardized conditions of measurements are needed for sensor materials investigation and sensor arrays training.

To solve above problems, an experimental system is required that solve several technical tasks: preparation of multicomponent vapor mixtures with specified concentrations of analytes, registration and measurement of optical properties of sensor materials in the presence and absence of analytes, well-ordered storage the results, conditions of measurements and settings of apparatus. In this paper, an experimental setup that satisfies conditions mentioned above is described and some results of measurements are presented.

## Hardware

The structure diagram of the system is shown in the figure 1. The system includes two main subsystems: a subsystem for preparation and control of gas-vapor mixtures and a subsystem of registering the optical responses of sensor materials. The previous version of the system was described in (Khlebunov et al., 2007).

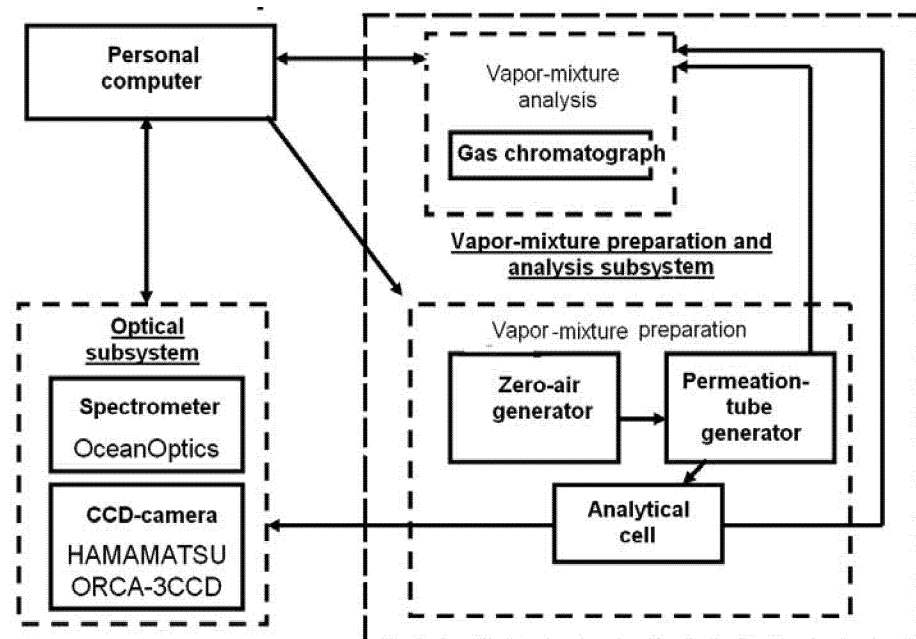


Figure 1 – The structure of the experimental system

### Subsystem for vapor-mixture preparation and analysis

The subsystem includes: a compressor S-50 (Ekom, Czech Republic), a zero air generator HZPA-3500 (Parker Balston, USA), a permeation-tube generator Microgas F-46 (Intera, Russia), a gas chromatograph Crystal 5000.2 (Chromatec, Russia), an automatic gas batcher (Chromatec, Russia), valves for directing gas flows (Camozzi, Italia), and an analytical cell.

The main part of the subsystem is the vapor mixtures generator Microgas F-46. This equipment enables multicomponent vapor mixtures with the given concentration of each component to be prepared. The maximum number of different components in the mixture is 6. The range of concentrations for the majority of volatile organic compounds (VOCs) is between 200 ppb and 500 ppm. This equipment satisfies the Russian national standard for the gas mixture preparation. The equipment can work both with either permeation tubes or cylinder gas mixtures. Calibrated permeation tubes were received from the All Russian research institute of metrology (VNIIM, St. Petersburg). If necessary, the permeation tubes may be calibrated in our laboratory according to the standard method. Therefore, the gas-vapor mixtures used for determining functional characteristics of the sensor materials are certified.

In the gas scheme, ambient air is used in the role of carrier gas. The zero air generator (ZAG) of thermo-catalytic type is used for drying the air and removing organic impurities. Purified air is directed to the input of the mixture generator or to the input of the analytical cell for expulsion.

The gas chromatograph is used for the control of gas mixtures, the impermeability of compounds and also for the fast calibration of permeation tubes in additional points of a calibration curve. The extraction of gas samples into the chromatograph is carried out by means of an automatic gas injector.

The direction of gas flows is controlled by automatic three-way valves. The position of the valves determines the mode of operation of the gas scheme. Gas scheme has three main modes. In the mode "Analysis" a gas vapor mixture is directed into the analytical cell where a sample of sensor material or a sensor array are placed. In the mode "Expulsion" the air from the ZAG is moved to the input of the analytical cell for removing the traces of the previous mixture. In the mode "Control" the mixture is directed to the chromatograph for the analysis.

A sample of a sensor material is placed into the analytical cell, which is a hermetical metal container from stainless steel with the dimensions 100x50x30mm (figure 2).



*Figure 2 – Analytical cell*

One of the side panels of the container is made in the form of flange which allows one to promptly change samples of sensor materials. The walls of the container have several

orifices for supplying and removing the gas-vapor mixes and for placing the temperature and pressure sensors. The quartz glasses are installed in the top and bottom walls of the container, that allows one to use various light sources to excite samples and to read their responses. The flow of a gas mixture through the analytical cell occurs in two modes: in a dynamic mode when the mixture goes through the cell at a constant flow rate, and in a static mode when the mixture is trapped in the cell. The elements of the subsystem are connected by means of teflon capillary tubes.

### **Optical subsystem**

Optical subsystem serves to register following optical characteristics of sensor materials: fluorescence spectra, reflection spectra, fluorescent images and images in reflected light. The optical subsystem allows one to register optical characteristics and their change in time. This subsystem includes: an eight-channel fiber optic spectrometer S 2000 (Ocean Optics, USA), a CCD-camera C-7780-20 (Hamamatsu, Japan), an automatic monochromator Polychrome 5 (Till Photonics, Germany), LEDs connected with optical fibers (Ocean Optics, USA) and a microscope Olympus CX-41 (Olympus, Japan).

The spectral range of the spectrometer is between 300 nm and 900 nm, the optical resolution is 2 nm. These parameters are sufficient for registering wide spectral bands of the majority of dyes. The spectrometer allows changes of spectra with the time resolution from 10 ms to 3600 sec to be registered.

Scientific grade CCD-camera is used for registering the images of the samples. The camera contains 3 cooled CCD-chips, one per color channel. This gives an opportunity to get color images of the objects which have high spatial and color resolution and also the high signal-to-noise ratio. The spectral range of the camera is between 400 nm and 800 nm. The camera enables the image changes with the time resolution from 0,6 seconds to 10 seconds to be register. The camera with the long-focus objective allows optical properties of the samples with the size not less than 2 mm to be registered.

For excitation of fluorescence in sensor materials different sources of light are used. Automatic monochromator permits monochromatic emission in the range between 320 nm and 680 nm to be obtained. Additionally, there is a set of LEDs, with the emission wavelengths of 380, 470, 518, and 635 nm. Wide range of fluorescent dyes can be excited with this set of light sources.

Only signals from samples with the relatively large dimensions can be registered with fiber optic spectrometer and CCD-camera with the long-focus objective. But, it is extremely important to have an ability to work with micro samples and single microspheres. For this purposes a fluorescent microscope is used. The construction allows the analytical cell to be placed on the objective table of the microscope. As a result, the kinetics of changes in the optical properties of microsamples during their interaction with analytes can be registered.

## Investigation of sensor materials

Materials consisted of silica microspheres doped with fluorescein dye were made and studied. Silica microparticles Lichrospher Si with sphere diameter 10 micrometers and 10 nm pores were used. Material was made by the following method: a droplet of water solution containing 4 % of polyvinylpyrrolidone PVP (Fluka, Germany) and 2% of silica microspheres was deposited on a polyether substrate and drayed during 15 hours at the room temperature, after drying a layer of microspheres was formed. Ethanol (Scharlau Chemie, Spain) solution containing  $10^{-4}$  M fluorescein dye (Alldrich, Germany) was deposited on the microspheres layer.

The fluorescent image of a single silica microparticle with immobilized fluorescein obtained with a scanning-confocal microscope Nikon Eclipse C1Plus is shown in figure 3.

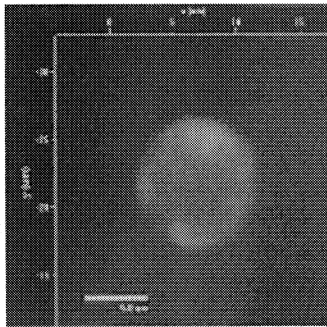


Figure 3 – Fluorescent image of Silasorb microspheres doped with fluorescein

The fluorescence spectrum of the sensor layer measured with a spectrofluorophotometer Shimadzu RF-5301 PC is shown in figure 4.

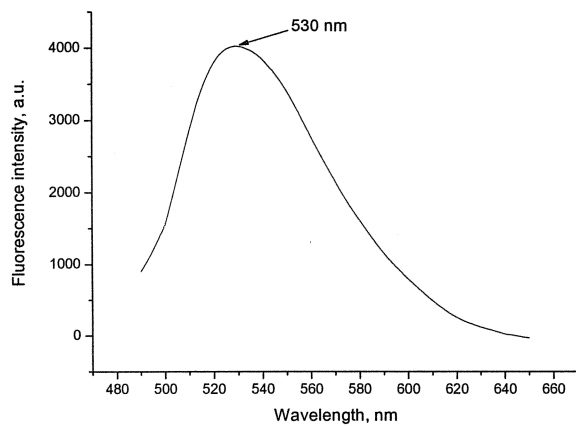


Figure 4 – Fluorescence spectrum of the layer of silica microspheres and PVP doped with fluorescein dye

Figure 5 shows the kinetics of spectral changes obtained with a fiber optic spectrometer Ocean Optics S2000. A sample of sensor material was placed in air flow with 20 ppm of ammonia. Signal was registered at the fluorescence maximum wavelength 530 nm. LED with wavelength 460 nm was used as an excitation source.

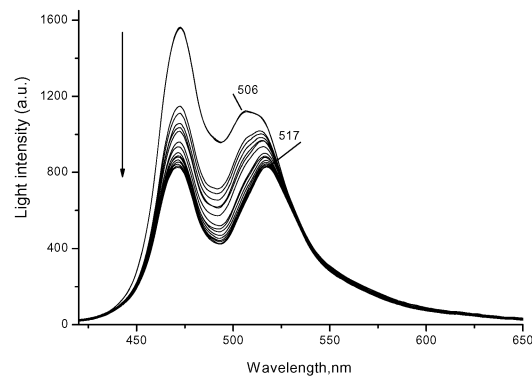


Figure 5 – Changes in light intensity of material in the presence of 20 ppm ammonia

Each spectrum in Figure 5 is complicated and consists of spectrum of excitation light transmitted through the sample and spectrum of fluorescence light. Presence of ammonia leads to decrease of transition and fluorescence light intensity.

The sensor array containing four sensor elements was made from silica microparticles and four dyes fluorescein, acriflavine (Aldrich, Germany), eozine (Aldrich, Germany) and 9-DTAA (2,7-Dimethyl-9-(Ditolylamino)acridine, molecular structure and synthesis method can be found in Sazhnikov et al., (2006)) according the method described above. The fluorescence spectra of the sensor array elements are presented in figure 5.

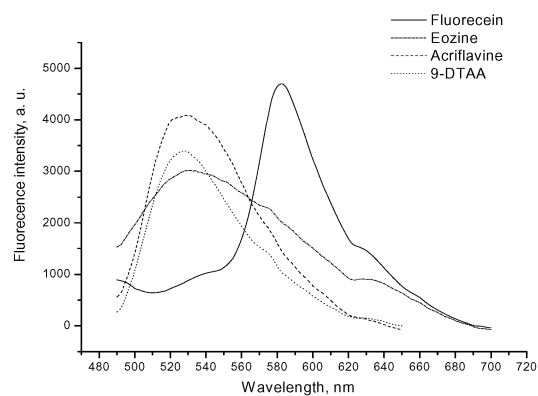


Figure 5 – Fluorescence spectra of the sensor array

Response of the array to ammonia is shown in figure 6. The array was placed in air flow with 20 ppm of ammonia. UV-LEDs with wavelength 380 nm were used as an excitation source.

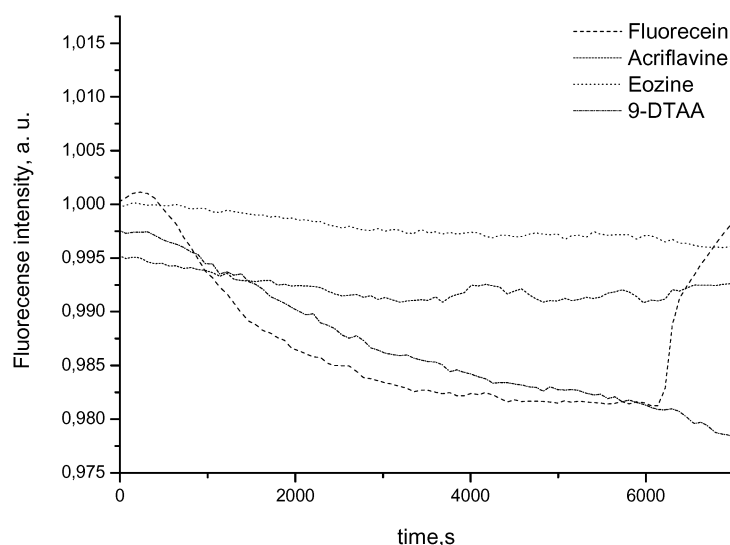


Figure 6 – Response of sensor elements in the presence of 20 ppm of ammonia

It is clear from the figure that only fluorescein and 9-DTAA are significantly sensitive to ammonia.

## Conclusion

The setup described above has abilities to create multicomponent vapor-gas mixtures of a large number of VOCs with well defined analyte concentrations, to measure characteristics of optical sensor materials and to store obtained data in a database. This system is suitable for study various optical sensor materials, for example, materials based on dye-doped microparticles.

The spectral-luminescence properties of a dye on the microparticle surface and their dependence on the microparticle material and the surface chemical groups can be obtained with the system. Analysis of this data allows one to characterize optical sensor materials.

Functional characteristics of optical sensor materials can be evaluated from the kinetic dependencies of optical properties induced by action of an analyte. The system permits dependencies of functional characteristics on analyte and dye nature as well as on their concentrations and matrix type to be measured.

The described setup can be used for fast screening of sensor materials and fast selection of sensor materials suitable for a given analyte. The setup also allows electronic noses based on optical sensor materials to be trained.

## References

- Borisov S.M., O. S. Wolfbeis, 2008, *Chem. Rev.*, 108, 423
- Brian, 2004, *Proc. SPIE*, 5588, 59.
- Dickinson, T.A., J. White, J.S. Kauer and D.R. Walt, 1996, *Nature*, 382, 697.
- Khlebunov, A.A., D.S. Ionov, I.V. Savenkov, V.A. Sazhnikov, V.M. Aristarkhov, M.V. Alfimov, 2007, *Book of Abstracts ISOEN-2007*, St.-Peterburg, May 3-5, 217.
- Mc Donagh, C., C.S. Burke and B.D. McCraith, 2008, *Chem. Rev.*, 108, 400.
- Pearce, T.C., S.S. Shiffman, H.T. Nagle and J.W. Gardner, 2003, *Handbook of Machine Olfaction: Electronic Nose Technology*, Wiley-VCH, Weinheim.
- Plotnikov, V.G., V.A. Sazhnikov, M.V. Alfimov, 2007, *High Energy Chem.*, 41, 299.
- Sazhnikov V.A., A.A. Khlebunov., M.V. Alfimov, 2006, *High Energy Chem.*, 41, 25.
- Shinar, R., B. Choudhury, Z. Zhou, H.-S. Wu, L. Tabatabai, J. Shinar and M. Cullum
- Tam, J.M., L. Song and D.R. Walt, 2005, *Talanta*, 67, 498.
- Wu, W.-B., M.-L. Wang, Y.-M. Sun, W. Huang, Y.P. Cui, C.-X. Xu, 2008, *J. Phys. and Chem.*, 69, 76.