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FINAL REPORT

CHEMICAL SENSORS BASED ON IR SPECTROSCOPY AND SURFACE-MODIFIED WAVEGUIDES

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Tech. POCs / UNM: Prof. Gabriel P. Lopez
Dept. of Chemical and Nuclear Engineering
and Department of Chemistry
University of New Mexico
Albuquerque, NM 87131
net: gplopez@unm.edu

Prof. Thomas Niemczyk
Department of Chemistry
University of New Mexico
Albuquerque, NM 87131

Tech. POCs / NASA: Dr. John C. Sager, Ph.D
NASA, MD-RES
Kennedy Space Center, FL 32899
Telephone: (407) 853-5142

Dr. Ken Poimboeuf
NASA, BE-TPO
KSC, FL 32899
Telephone: (407) 867-2780

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Sol-gel processing techniques have been used to apply thin porous films to the surfaces of planar infrared (IR) waveguides to produce widely useful chemical sensors. The thin-film coating serves to diminish the concentration of water and increase the concentration of the analyte in the region probed by the evanescent IR wave. These porous films are composed of silica, and therefore, conventional silica surface modification techniques can be used to give the surface a specific functional character. The sol-gel film was surface-modified to make the film highly hydrophobic. These sensors were shown to be capable of detecting non-polar organic analytes, such as benzonitrile, in aqueous solution with detection limits in the ppb range. Further, these porous sol-gel structures allow the analytes to diffuse into and out of the films rapidly, thus reaching equilibrium in less than ten seconds. These sensors are unique because of the fact that their operation is based on the measurement of an IR absorption spectrum. Thus, these sensors are able to identify the analytes as well as measure concentration with high sensitivity. These developments have been documented in previous reports and publications.

Recently, we have also targeted detection of the *polar* organic molecules acetone and isopropanol in aqueous solution. Polar organics are widely used in industrial and chemical processes, hence it is of interest to monitor their presence in effluents or decontamination process flows. Although large improvements in detection limits were expected with non-polar organic molecules in aqueous solutions using very hydrophobic porous sol-gel films on silicon attenuated total reflectance (Si ATR) waveguides, it was not as clear what the detection enhancements might be for polar organic molecules. This report describes the use of modified sol-gel-coated Si ATR sensors for trace detection and quantitation of small polar organic molecules in aqueous solutions.

The detection of both acetone and isopropanol molecules in aqueous solution has been previously reported for chalcogenide fiber optic sensors. In these reports, the waveguide fibers were placed directly into the sample solution. The analyte detection limits reported were in the 2 - 5 % range, limited largely by the small volume of sample queried by the evanescent wave and the strong absorption of water in the mid-infrared region. In the work described here, a surface-modified, sol-gel-coated planar mid-infrared waveguide was used to detect these analytes. In contrast to our previous studies with benzonitrile in aqueous solution, the porous sol-gel film used for this application was not completely hydrophobic. The sol-gel film was produced using a mixture of ethyltriethoxysilane and tetraethoxysilane and the surface modification was carried out using trimethylchlorosilane. We have demonstrated that this film concentrates the target polar analytes from aqueous solution in the region probed by the evanescent wave to improve detection limits by as much as a factor of 450. When the waveguide technology is combined with partial least squares (PLS) multivariate calibration methods and statistically designed calibration experiments, these coated Si waveguides yield detection limits that are over three orders of magnitude lower for acetone and more than two orders of magnitude lower for isopropanol than those found for univariate methods applied to aqueous solutions on bare Si waveguides of the same dimensions. The resulting standard errors of prediction for acetone and isopropanol molecules in aqueous solutions are below 10 ppm. Further, we have shown that these surface-modified sol-gel-coated sensors can be used to perform simultaneous quantitative determinations of multiple analytes in dilute aqueous mixtures. This is a direct consequence of the fact that infrared spectral data, where each analyte has a unique signature, are used as the basis of the sensing operation.

In another set of studies that were completed, we were able to identify the factors that limit the sensitivity and detection limits of these new infrared sensors. Using these results, we are able to identify methods to further reduce the detection limits. By the use of multiple repeat samples, the detection limits for these sensors are shown to be limited by the signal-to-noise ratios of the spectral data collected, rather that sensor drifts, or reference errors. Reference errors are particularly difficult to eliminate when preparing low concentration solutions of volatile analytes such as acetone and isopropanol.

In summary, the surface-modified, sol-gel-coated Si waveguide sensor coupled with multivariate partial least squares calibration methods allowed approximately three orders of magnitude improvement in detection limits for acetone when compared to previously published sensor results. The comparable improvement for isopropanol in aqueous solution was over two orders of magnitude. Studies performed on mixtures of acetone and isopropanol in water confirmed that quantitative analyses could be performed on these mixture systems with cross-validated standard errors of prediction (CVSEP) of 0.5 and 8.7 ppm, respectively. Using three times the CVSEP as an estimate of the detection limit translates to detection limits of 1.5 and 26 ppm for acetone and isopropanol, respectively.

This application of the partial least squares algorithm to spectral data produced by these sensors was a good example of how PLS can generally provide excellent quantitative analysis precision, but accomplishing qualitative spectral interpretation from such a model can be more difficult. For example, although we have achieved sensitivity in the ppm range for isopropanol detection in aqueous solutions using the IR waveguide sensors described above, we were not able to initially understand on what the calibration was based. The interpretation of PLS loading vectors obtained from calibrations involving orthogonally designed solutions of acetone and isopropanol in water resulted, at least initially, in an incorrect understanding of the mechanism for the IR detection of isopropanol on these sensors. Examination of the loading vectors from the PLS calibration model would suggest that the spectral calibration is based largely on the interaction of the isopropanol with the surface modifier of the sol-gel waveguide coating. However, a classical least squares (CLS) analysis of the data shows clearly that this interaction is not a significant source of the spectral calibration, but rather the calibration is primarily due to the spectroscopic signal of the isopropanol analyte. In this case, the misleading qualitative interpretation of the PLS model was the result of the spectral variation being dominated by the effects of spectrometer drift. CLS can overcome this problem if a parameter is included in the CLS calibration that adequately represents the drift. In the example discussed here, time of spectral data collection proved an appropriate drift-related parameter that can be added to the CLS calibration concentration model in order to provide the qualitative information needed to correctly interpret the spectral data. We have been able to generalize this result, i.e. have discovered new methods to incorporate instrument drift into multivariate calibration algorithms to improve the quantitative calibration results.