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FIBER-OPTIC SURFACE-ENHANCED RAMAN SYSTEM FOR FIELD SCREENING OF HAZARDOUS COMPOUNDS*

T. L. Ferrell E. T. Arakawa R. B. Gammage D. R. James
J. P. Goudonnet R. C. Reddick J. W. Haas E. A. Wachter
Health and Safety Research Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6123

ABSTRACT

Surface-enhanced Raman scattering permits identification of compounds adsorbed onto a metal microbase that is microlithographically produced with submicron resolution. Less than one percent of a monolayer of a Raman active target compound offers a high signal-to-noise ratio. By depositing the microbase on the exterior of a fiber optic cable, convenient field screening or monitoring is permitted.

By using highly effective microbases, it is possible to reduce laser power requirements sufficiently to allow an economical, but complete, system to be housed in a suitcase. We shall present details of a SERS system of this type and shall show data on samples of interest in the screening of hazardous compounds.

Key words: Raman scattering, hazardous compounds

INTRODUCTION

There is a need for rapid and reliable on-site qualitative analysis of aqueous samples taken from aquifers, toxic waste sites, industrial and agricultural areas, and other environmentally sensitive locations. For many targeted compounds, the adsorption isotherm permits collection on a surface with suitable filters. Analysis of the spectra of the compounds, including deconvolution analysis for complex mixtures, can be carried out for a variety of methods that are sensitive to ultralow levels. Reliability of the analysis is affected by sample degradation for the relatively slower analytical techniques, and the aqueous samples pose limits for some methods such as infrared absorption spectroscopy. Surface-enhanced Raman spectroscopy (SERS) is a relatively new tool for analytical chemistry which fills a gap in the methods of attack available for detection of concentrations of parts per billion.

Raman spectroscopy identifies molecules by their vibrational and rotational spectrum, as does infrared absorption spectroscopy. However, in Raman spectroscopy one uses visible light, the Raman spectra appearing as wavelength shifts from the wavelength of the incident light. This requires that the incident wavelength be taken out of the scattered light by filtering or dispersion. Due to the fact that only a small fraction of the light is Raman shifted, one needs good filters or a double monochromator or an optimized combination. SERS provides signals comparable to those obtained in Raman scattering from solutions, but detects a factor of over one million less in the number of molecules. For instance, one reason for this is that silver microstructures (upon which the molecules are adsorbed) actually concentrate the electric field of the incident light. Since the scattering is proportional to the square of the field, this produces a scattering cross section that is adequately large. The high reflectivity of silver and the size and shape of the microstructures are important in optimizing the signal. We have produced several different types of microstructures using methods common to the semiconductor industry. Our results demonstrate a high performance level for silver microneedles evaporated at near grazing incidence onto an evaporated calcium fluoride surface. Electron micrographs and optical absorbance data have been taken in modeling our samples. Good agreement has been obtained with electrodynamical calculations which model the silver microneedles as prolate spheroids.

EXPERIMENTAL FEATURES

For on-site measurements it would be desirable to utilize fiber optic cables that can be used as extended probes or left over a period of time for monitoring purposes. We have demonstrated that SERS can be carried out using a totally internally reflected laser beam and have deposited several different types of microstructures on a prism base and on optical fibers. It now seems desirable to attempt to perform stimulated SERS by increasing the power density through improvement of the microstructures and use of higher power lasers. The data we have obtained to date using internal reflection show an adequate signal-to-noise ratio, but further investigation is warranted.

Due to the importance of the shapes of the microstructures, we have carried out exhaustive analysis of the geometries available for practicable systems. We have employed scanning-tunneling electron microscopy to obtain shape-effect data.

We have examined a number of compounds to test the performance of SERS. While it is more difficult to detect many of the more symmetric molecules--and in certain cases fluorescence contributes to the noise--a wide range of compounds of interest have demonstrated adequately large SERS cross-sections. Reproducibility problems have been encountered which need further research.

SUMMARY

SERS can be utilized in a convenient, rapid, and reliable form for a variety of on-site applications involving ultralow levels of targeted compounds. Some degree of development remains to be carried out in order to provide better reproducibility.

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