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Selective-Ultratrace Detection of Metal Ions with SERS

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We report the results from experiments involving the detection of metal ions with a Surface-Enhanced Raman Spectroscopic indicator (SERS indicator). Comparisons of metals showed that the SERS effect can be used to selectively detect metal ions according to their ionic radius. We determined a resolving power for separating the alkaline earth series. The results indicate that the resolving power of the SERS approach is superior to that of absorption spectroscopy. Quantitatively, under our experimental conditions, we found a detection limit of 270 ppb for Pb^{2+} and 85 ppb for Cu^{2+} with the indicator Eriochrome Black T.

Index Headings: SERS; Ultrasensitive detection; Metal ions; Instrumentation, Raman spectroscopy; Lasers; Eriochrome Black T.

INTRODUCTION

Surface-Enhanced Raman Spectroscopy (SERS) has been shown to be an ultrasensitive technique.[1-3] The ultrasensitivity has been utilized in the spectroscopic study of monolayer and submonolayer quantities of organic compounds, organometallic compounds, and inorganic anions on metal surfaces. Examples of analytical applications of SERS are the trace detection of dyes[4] and nucleic acids.[5] One important class of compounds which has not been detected by SERS is metal ions. Metals ions are challenging since as a single atom they do not possess a vibrational spectrum and, therefore, cannot be directly detected with Raman spectroscopy.

With the current interest in remote fiber-optic sensors, the ultrasensitivity of SERS is being explored as a possible spectroscopic technique for optical fiber sensors. Direct detection of the analyte has been the scheme proposed for the current SERS-based fiber-optic sensors. Examples of sensors proposed around SERS technology are organochloride pesticides,[6] various hazardous aromatic compounds adsorbed to surfaces,[7] electrochemically adsorbed chloropyridines,[8] and pyridine.[8,9] We report here a new approach to SERS sensors which utilizes a Raman indicator. In this case the indicator is Eriochrome Black T (EBT). EBT has been explored by Seitz and co-workers as the basis for an energy transfer/fluorescence quenching fiber-optic sensor.[10] The advantage of SERS-based sensors is that the information content of vibrational spectra is much larger than electronic spectra, and when SERS is combined with resonance enhancement the sensitivity of SERRS (Surface-Enhanced Resonance Raman Spectroscopy) equals that of fluorescence spectroscopy.[2] Furthermore, the difficult problem of measuring absolute intensities is solved since the indicator is its own internal standard and a subtraction technique using $I_{complexed\ indicator} - I_{uncomplexed\ indicator}$ can be used.

Our goal in this study is to show that it is possible to overcome the hinderance of electrochemical SERS probes by utilizing an adsorbed indicator to chelate the analyte with the surface. We also demonstrate the sensitivity advantage of using a resonantly enhanced indicator to signal the presence of a nonresonant analyte.

EXPERIMENTAL

The SERS substrates were fabricated from 1-in. glass squares cut from microscope glass slides. The slides were initially cleaned with concentrated ammonium hydroxide, then rf sputtered with a Harrick PDC-3XG plasma cleaner to remove any remaining impurities. The SERS surface was produced by depositing 250 nm CaF_2 (optical-grade CaF_2, Aesar) and 50 nm Ag (99.99%, Aldrich) at 4×10^{-6} mbar using an Edwards E306A Vacuum Coating System. The substrates were stored under vacuum in the coating unit until they were used for spectroscopy.

Eriochrome Black T (80% pure, Aldrich) was purified by recrystallization of the dimethylammonium salt. This procedure was found to be necessary to obtain good results and is outlined in Ref. 11. All solutions were prepared with Millipore water or spectral-grade acetone (Baker). All aqueous solutions were buffered to pH 9 with NH_4Cl or $NaHCO_3$.

Raman spectra were collected and stored with a 386 microcomputer interfaced to a Jobin-Yvon Mole 1000 double monochromator, a thermoelectrically cooled RCA 31034 PMT, and Ortec photon-counting electronics. Either a Spectra-Physics 2016 or a 2025 Kr^+ laser provided 531-nm light for resonant excitation of EBT. The laser power was adjusted to provide 20 mW at the sample after passing through a 531-nm interference filter. The incident angle of the laser light to the substrate was 45°. A backscattering geometry was used with the exciting light focused on the sample through a cylindrical lens to decrease the power density. The sample was spun at 1800 rpm to eliminate laser-induced damage and to provide an average of the surface spectrum. An F2 collection lens was used to focus the Raman light on the monochromator slits. The slits were adjusted to provide a 5-cm^{-1} bandpass.

Group II metals and Cu^{2+} samples were prepared for analysis by applying 150 μL of an aqueous buffer solution of metal + EBT to the SERS substrate. The EBT concentration was varied depending on the experiment. A second procedure was tested for Pb^{2+} samples. In this case the EBT/metal complex was extracted with 1-pentanol (Aldrich), the pentanol was evaporated, and the residue was redissolved in methanol. Fifty μL of the methanol solution was applied to the SERS substrate. In all cases the analyte solution was applied by spin
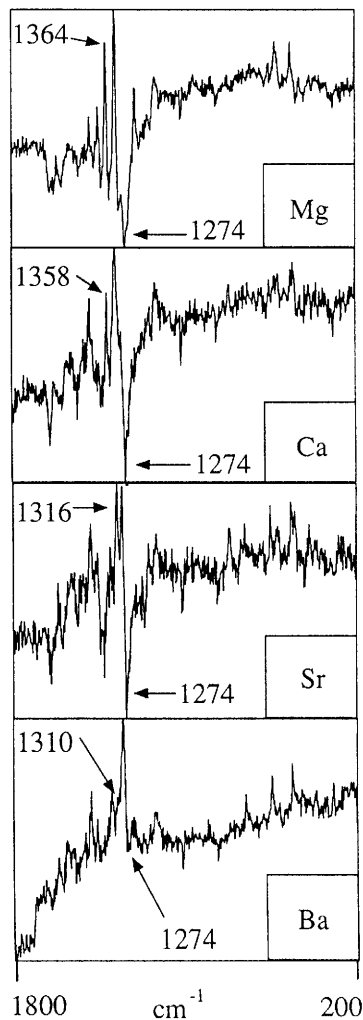
APPLIED SPECTROSCOPY

FIG. 1. The difference spectra of EBT/alkaline earth SERRS spectra minus the SERRS spectrum of EBT. The spectra were taken with 20 mW of 531-nm laser excitation. The subtraction was from a blank taken under the same conditions as the EBT/metal complex spectra. The 1274-cm⁻¹ band disappears in the complex, and a strong metal-dependent 1364–1310 cm⁻¹ band appears.

coating to provide an even coverage. A slight vacuum was maintained during the coating procedure to facilitate solvent evaporation.

The EBT coverage was determined by absorbance spectroscopy of solutions containing dissolved EBT rinsed from 10 SERS substrates. The dissolution of EBT was carried out with a pH 9 buffer solution. We determined a molar absorptivity of 18,300 at 542 nm. This is in reasonable agreement with literature values for an equilibrium of HL^{2-} and L^{3-}.[12] Our coating procedure was found to produce an average coverage of 2×10^{14} molecules/cm^2 with a 1.8×10^{-3} M EBT aqueous solution.

RESULTS AND DISCUSSION

Figure 1 illustrates the qualitative aspects of SERRS detection of metals. We chose to use the alkaline earth metals as a test case since they possess very similar chemical properties. The spectra in Fig. 1 are subtractions of EBT/metal minus EBT on rough silver substrates. The strongest bands in the SERRS spectrum of EBT are the stretches associated with the diazo nitrogens.[13] It can also
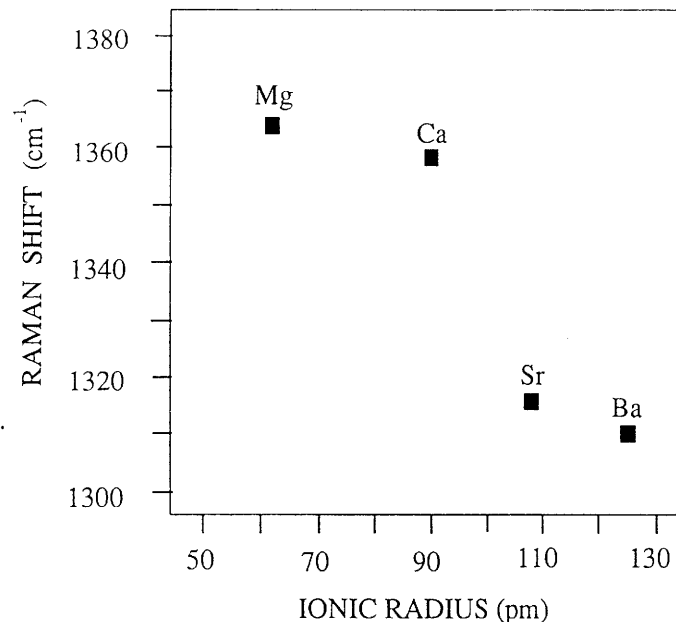

FIG. 2. A plot of the frequency of the metal-dependent SERRS band and ionic radius. The ionic radii were taken from Ref. 13.

be seen that in the low-wavenumber region several weak unique bands appear in the metal complex. The most significant differences are the loss of the 1274-cm⁻¹ band and the appearance of a metal-dependent band between 1364 and 1310 cm⁻¹. The shift of the metal-dependent band can be correlated with the ionic radius. Figure 2 shows a plot of splitting vs. ionic radii for the alkaline earths. The ionic radii were taken from Ref. 14, and a coordination number of 6 was assumed. The selectivity advantage for SERS indicators over absorption spectroscopy can be seen in Table I. We defined the resolving power as

$$R = \text{(peak separation)/FWHM.} \qquad (1)$$

With respect to the Rayleigh criterion for resolution this means that bands with $R > 1$ will be resolved. It can be seen that for Mg^{2+} versus Ca^{2+}, Sr^{2+}, and Ba^{2+} none of the EBT/metal absorption spectra would be resolved. On the other hand, with SEERS all spectra except Mg^{2+}/ EBT-Ca^{2+}/EBT can be resolved.

Our first quantitative test of SERRS indicators was the detection of Pb^{2+}. Pb was chosen since it represents an environmental hazard. Figure 3 shows the SERRS spectrum of the EBT/Pb^{2+} complex. It was found that the most significant change upon chelation was the disappearance of the 1274-cm⁻¹ band, and the 1325-cm⁻¹ band gave the best results for Pb^{2+} concentration measurements. Figure 4 shows a plot of the 1274-cm⁻¹ band

TABLE I. Comparison of SERRS and absorption spectroscopy.

	Resolving power	
Metals	SERRS[a]	Absorption spectroscopy[b]
Ca-Mg	0.40	0.01
Sr-Mg	3.22	0.22
Ba-Mg	3.57	0.30

[a] FWHM$_{SERRS}$ = 15 cm⁻¹.
[b] FWHM$_{ABS}$ = 180 nm.

FIG. 4. The SERRS concentration profile for Pb^{2+}. The detection limit is 270 ppb as determined by the point at which the S/N = 3. Data below the detection limit were not used in the linear regression. The error bars represent the relative error.
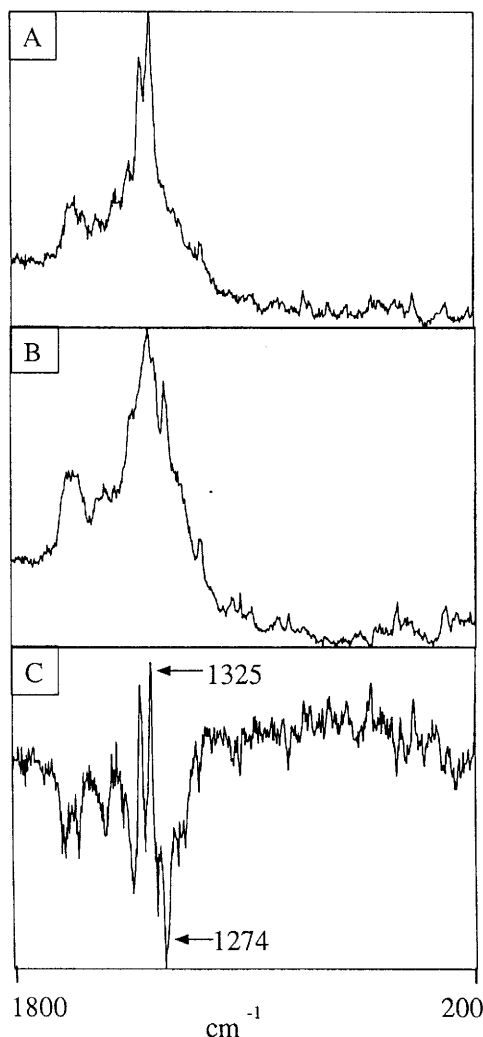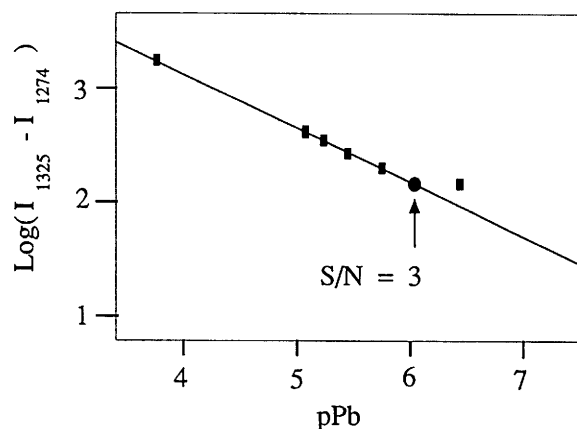
FIG. 3. SERRS spectra of (A) 2.7×10^{-4} M EBT and 2.7×10^{-4} M Pb^{2+}, and (B) 2.7×10^{-4} M EBT; C is the difference spectra of A minus B. The intensity difference between the 1325-cm^{-1} and 1274-cm^{-1} bands was found to produce good quantitative results for Pb determinations.

intensity minus the 1325 cm^{-1} band intensity vs. Pb^{2+} concentration. The EBT concentration was 2.7×10^{-4} M. The Pb^{2+} concentrations were made by standard dilutions of a 2.7×10^{-4} M $PbCl_2$ solution. The detection limit is determined as the point at which the intensity difference between the 1274- and 1325-cm^{-1} bands equals

$$C_L = 3 \times \sqrt{2(N_{1325})^2 + 2(N_{1274})^2} \qquad (2)$$

where C_L is the counts per second which correspond to the detection limit, and N is the shot noise for the blank (EBT) sample.[15] Our experimental detection limit for Pb^{2+} is 270 ppb. Our discussion on the qualitative aspects of SERRS indicators showed that the largest perturbations in the SERRS spectra of EBT/metal complexes occurred with small metal ions. Pb^{2+} is a medium-size ion and has an ionic radius of 119 pm (coordination number 6).[14] This resulted in a detection limit which does not represent the ultimate sensitivity for this technique. In particular, the metal-sensitive band at 1325-cm^{-1} for EBT/Pb^{2+} is convoluted with the 1331-cm^{-1} band of EBT. This lead to poor separation of bands and limited the sensitivity of our method.
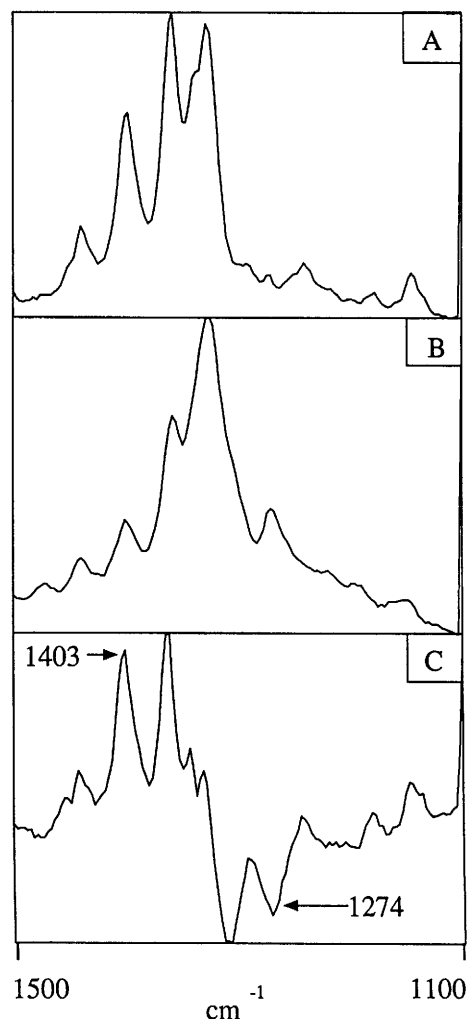

FIG. 5. SERRS spectra of (A) 1.8×10^{-4} M EBT and 1.8×10^{-4} M Cu^{2+}, and (B) 1.8×10^{-4} M EBT; C is the difference spectra of A minus B. The intensity difference between the 1403-cm^{-1} and 1274-cm^{-1} bands was found to produce good quantitative results for Cu determinations.
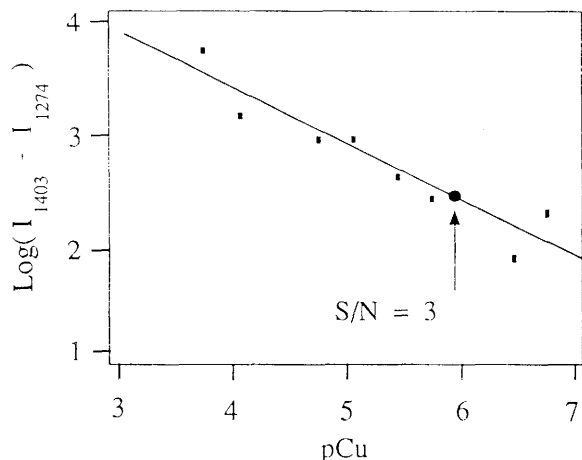
FIG. 6. The SERRS concentration profile for Cu^{2+}. The detection limit is 85 ppb as determined by the point at which the S/N = 3. Data below the detection limit were not used in the linear regression. The error bars represent the relative error.

A second study was performed with Cu^{2+} as the test analyte. The ionic radius of cupric ions is 0.73 pm.[14] Cu^{2+} produced much larger perturbations in the SERRS spectrum of EBT; therefore, a greater sensitivity was achieved. The SERRS bands used for the quantitative study are illustrated in Fig. 5. It was found that the bands at 1403 and 1274 cm^{-1} provided the best quantitative results. Figure 6 shows the concentration profile found for Cu/EBT. Data in Fig. 6 were obtained with an EBT concentration of 1.8×10^{-4} M. A standard dilution of 1.8×10^{-4} M $CuSO_4$ was used to form the concentration profile. The experimental detection limit for Cu^{2+} was found to be 85 ppb. The concentration profile is linear with respect to concentration of Cu^{2+}. Some variation in linearity might be expected due to the change in resonance condition which exists between the complexed and uncomplexed EBT. The scatter in the data (correlation = 0.9607) is most likely due to variations in the SERS substrates. For the Cu^{2+} determination the substrate coating procedure used a pH 9 buffered aqueous solution. This solution most likely caused some irregular oxidation of the Ag substrates. In particular, we have found that the small amounts of EBT can complex with the Ag substrates. This causes a large error since the complexed EBT also shows a decrease in the 1274-cm^{-1} band. The surface site of complexation is most likely an Ag^+ site. The degree of oxidation of the substrate will therefore cause a scattering of the data. The Pb^{2+} data support this assumption. The Pb^{2+} concentration profile was obtained by spin coating a methanol solution. Methanol would be expected to cause less oxidation of the Ag surface than the basic aqueous solution used in the Cu^{2+} experiment. It can be seen that the Pb^{2+} data are perfectly linear (correlation = 0.9997). The integration time

for this experiment was 3 s; therefore, an integration time of 100 s would reduce this down to 16 ppb.

CONCLUSIONS

We have demonstrated the ultrasensitivity of SERRS-based detection of metal ions. With practical integration times of 100 s, the sensitivity for the detection is about 16 ppb for Cu^{2+} and 50 ppb for Pb^{2+}. Furthermore, our instrument is designed for high-resolution Raman spectroscopy and does not have good light throughput characteristics. Reported sensitivities for direct detection of analytes are much lower. Carrabba et al. found for their best case, quinoline, a detection limit of 700 ppb.[9] In our work the increased sensitivity is a direct result from using an indicator which is resonantly enhanced. An improvement in our approach could be made by exploiting the high mass sensitivity of SERRS. For example, the mass sensitivity for cobalt phthalocyanine has been reported to be subattomole.[2] In our experiments the concentration measurement is based on measuring the difference between complexed and uncomplexed EBT. We found that we can measure differences down to 1:100 metal : EBT. Since the signals from 1.8×10^{-4} M EBT were large (13,000 cps), the sensitivity could be extended much lower than that found in this experiment by using lower initial concentrations of EBT. However, we found a problem with complexation of the EBT with sites on the Ag substrate. The obstacle which needs to be overcome is the fabrication of surfaces which are stabile and do not react with the indicator.

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