

Figure 3. Calibration curve for ethanol: (O) I_{peak} , $Y_I = -0.086 + 0.387X - 0.00110X^2$; (Δ) Q_{max} , $Y_Q = -0.372 + 6.27X - 0.0129X^2$.

greater in comparison to that shown in our previous report (saturation took place above 5 mM (0.023 wt %)). Q_{max} therefore was more suitable for measuring the wide range of ethanol concentration.

To determine a high ethanol concentration (X), we introduced a quadratic regression into the calibration. The regression curves for I_{peak} and Q_{max} are shown in Figure 3 by solid lines. The equation of the quadratic regression for I_{peak} (Y_I) was $Y_I = (-1.10 \times 10^{-3})X^2 + 0.387X - 0.0860$ ($r = 0.999$) and that for Q_{max} (Y_Q) was $Y_Q = -0.0129X^2 + 6.275X - 0.372$ ($r = 0.999$). Good correlations were obtained for both regression curves. Therefore, the ethanol concentration could be determined from 0 to 200 mM with Q_{max} and from 0 to about 150 mM with I_{peak} .

Stability. Continuous measurement was made automatically at 30 °C for 9 days. The response to the standard ethanol solution (10 mM) decreased linearly to about 90% of the initial value after 9 days. Although the decrease in sensor response was slightly larger than that reported previously (80% of the initial response after 1 month), this sensor system was more stable than the one that used AOD. The seemingly lesser stability seen here was caused by making continuous measurements for 9 days and repeating the measurement 10 times. Although the response of the sensor after 9 days had decreased to 90% of the initial response, the ethanol concentration could be determined over a long period (1 month or more) by the use of automatic calibration.

Determination of the Ethanol Concentration in Beers. Many types of beer are produced in the brewing industry. Recently, several new types that include "dry" beer, have been

developed because of changes in consumers' preferences (13). Because the attenuation limit for this type of beer differs from that of other beers, the monitoring and control of the brewing process is important for cost and quality control (1, 2, 14).

We evaluated the sensor system by measuring the ethanol concentrations in various beers: light, pilsner, black, and stout, which contained 2–7 wt % ethanol. Samples were analyzed after appropriate dilution. The results obtained by using this alcohol sensor system (C_X) were almost identical with those obtained by gas chromatography (C_Y) ($C_Y = 1.015C_X - 0.848$, $r = 0.994$).

Combined with an automatic sampling and diluting system, this sensor system should have a high capability for controlling the fermentation process because it is simple, stable, and more highly selective than the ethanol-measuring system that uses GLC and the AOD enzymatic method (7). This stable and selective alcohol sensor should prove useful in the many industries in which changes in ethanol concentrations are important factors in the production process.

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Stable Silver Substrate Prepared by the Nitric Acid Etching Method for a Surface-Enhanced Raman Scattering Study

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INTRODUCTION

When the technique now known as surface-enhanced Raman scattering (SERS) spectroscopy was discovered in 1974, most of the research reported in the following years was devoted to understanding the phenomenon itself (1–5). Only recently has there been intense interest in development of practically useful sample systems for the identification and

characterization of adsorbed species. This tendency seems to reveal that it is worthwhile to start analytical or catalytic studies on SERS active surfaces even without a final understanding of the SERS process. Practically attractive silver substrate forms on which the SERS effect is observed most intensely include colloidal silver, silver island films, silver films deposited on quartz or Teflon particles (6–8), and chemically reduced silver films on glass slides (9). In each case, the metal can be prepared independently of the sample. The sample

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can be mixed with a suspension of colloid or coated particles, or spotted on a plate containing silver island films. Colloidal silver has been the most widely employed form of silver, possibly because its preparation requires no specialized apparatus. Since some chemicals don't dissolve in water and many reactions don't occur in aqueous media, this sampling technique is apparently inadequate to adsorption or reaction mechanism studies in other solvent media. Additionally, silver sols are so prone to alter the surface morphological structure that useful SERS spectra can be deleteriously quenched. With respect to the aforementioned substrates, it has been difficult to obtain reproducible enhancements that are stable for long periods of time under elevated temperatures. These problems hinder widespread acceptance of SERS as a technique for mechanistic investigations.

In 1984, Wokaun et al. pointed out that pronounced SERS signals could be easily acquired by etching copper foils with concentrated nitric acid (10). They have demonstrated that the chemical etching method shows its potential to be developed into an analytical tool for routinely preparable substrate system for SERS study. As an extension of their studies, SERS results are presented in this work for several adsorbates on silver foils. In order to establish the versatility of our sampling technique, the Raman measurements were undertaken after the sample substrates had been exposed to different environmental conditions. To our knowledge, few reports have been made on the stability studies about the SERS effect on such simply prepared substrates up to now. The reason for using chemically etched silver foils as substrates can be pointed out. First, they are easily prepared by chemical techniques, which are simpler than the generation of properly roughened electrodes or electrochemically deposited surfaces and even simpler than the generation of metal colloidal particles with specific size range. Secondly, the costly instrumentation used to produce and characterize vacuum-deposited metal island films is not needed. Thirdly, a silver foil may suppress undesirable fluorescence so that sample purification is sometimes unnecessary. Finally, silver foils provide the possibility of rapid heat conduction under laser irradiation, therefore minimizing sample decomposition and surface morphological instability. To our surprise, such substrates show extraordinary stability under various environmental conditions. A good thermal stability of the surface enhancement factor is very important in order to apply SERS to catalytic studies, since many chemical reactions are undertaken at elevated temperatures. The importance need not be discussed in depth here.

EXPERIMENTAL SECTION

Instrumentation. Raman spectra were recorded with a SPEX-1403 Raman spectrometer. The incident excitation wavelength was 647.1 nm from a Kr laser source, with output powers 100–200 mW. A back-scattering geometry in air was used for all samples. The Raman band intensities are reported in $\text{counts}\cdot\text{s}^{-1}\cdot\text{mW}^{-1}$ to account for the different laser powers and integration times. In order to ensure that there is no laser-induced change in the SERS spectra, the foil was spun during the measurement. Spinning can also average the detecting adsorbate thickness.

Procedures. All reagents were purchased from Aldrich Chemical Corp. and were reagent grade. A 0.025 mm thick silver foil was immersed into vigorously agitated 3.5 M HNO_3 at ambient temperature, for about 2–3 min until the foil became a milky surface. This procedure created a sponge-type surface with abundant roughness features on a 10–100-nm scale, as shown by scanning electron micrographs. After etching, the foil was thoroughly rinsed with distilled water and dried in air. The roughened foil was ready for sample doping. The procedure is similar to the etching method for copper development by Wokaun et al., except for the concentration of HNO_3 (10). It was reported that HNO_3 with a concentration of 2 M could create surface

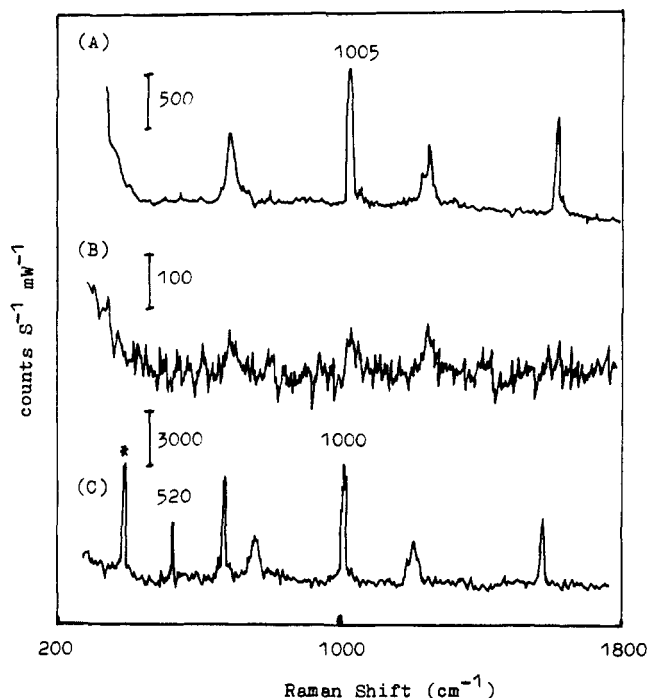


Figure 1. (A) SERS spectrum of benzyl disulfide (BDS) on a HNO_3 -etched silver foil that had been heated at 130 °C for 1 h before sample doping. (B) SERS spectrum of benzyl disulfide on a Ag/CaF_2 substrate that had been heated at 130 °C for 1 h before sample doping. (C) Normal Raman spectrum of benzyl disulfide in CHCl_3 (0.5 M). Asterisk denotes a solvent band.

roughness on copper. But we found that only concentrated HNO_3 (>3.5 M) could roughen silver effectively. Another surface morphology was used for the purpose of comparison: calcium fluoride roughened films overcoated with silver. Calcium fluoride and silver were vapor-deposited onto a 1-in.² glass slide in a cryopumped vacuum system at pressures of approximately 10^{-6} Torr.

The adsorbates were initially dissolved in ethanol. A silver foil roughened with HNO_3 was dipped into the adsorbate solution for approximately 30 s. As reported by Garoff et al., this method results in rather uniform coverage of the adsorbate, controlled by the concentration of the adsorbate in solution (11). The dipping technique has also been shown to yield reproducible coverages in the monolayer range, and for physisorbed molecules this technique results in a coverage that is relatively insensitive to the substrate material. Since the saturated surface was found to be attained with a doping solution concentration of 0.001 M (9, 12), our doping solution was kept at 0.001 M. This method appeared to provide good SERS spectra for adsorbates that could be dissolved in volatile solvents. After withdrawing, the excess liquid was blown off with nitrogen.

RESULTS AND DISCUSSION

1. Benzyl Disulfide (BDS) and 2-Mercaptobenzimidazole (MBI): Heat Endurance Tests. An excellent SERS spectrum was obtained from monolayer BDS on the HNO_3 -roughened Ag foil, which had been heated at 130 °C for 1 h before sample doping, as shown in Figure 1A. For comparative purposes, the Raman spectrum on the Ag/CaF_2 substrate, which had been treated under the same conditions, is presented in Figure 1B. The band at 520 cm^{-1} , which is due to S–S stretching, exists in the normal Raman spectrum of BDS in chloroform solution but disappears in the SERS spectra. This phenomenon has been reported by Sandroff and Herschbach (13). By comparing the SERS spectrum of benzyl disulfide with that of benzyl sulfide, they proposed that the S–S linkage was readily cleaved to form mercaptide species on Ag surfaces. Though more detailed studies are required to produce an accurate measurement of the surface en-

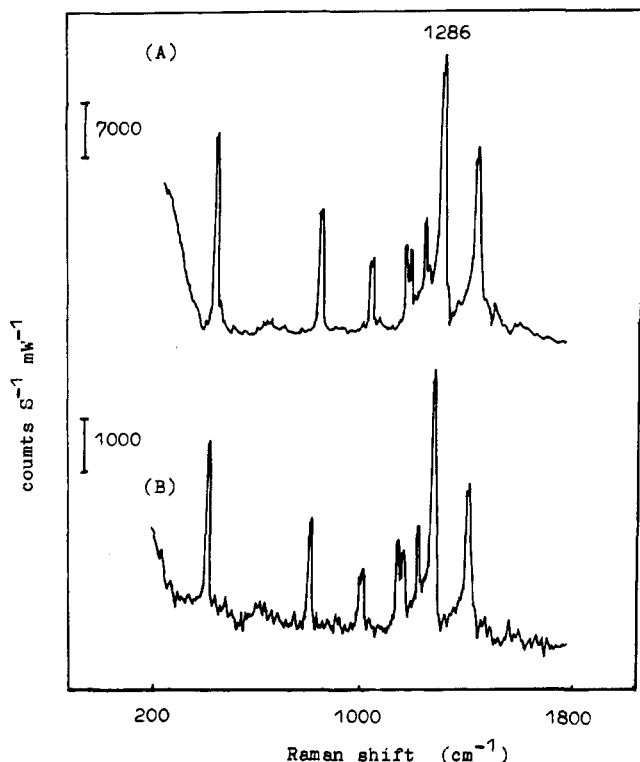


Figure 2. SERS spectra of 2-mercaptobenzimidazole (MBI) (A) on a HNO_3 -etched silver foil and (B) on a vacuum-deposited Ag/CaF_2 substrate.

enhancement factor (EF), a semiquantitative estimate can be provided by comparing the intensity of the sharp ring mode at the 1005-cm^{-1} band on the HNO_3 roughened silver foil with that observed for BDS scatters in solution under the same experimental conditions. When monolayer coverage at the surface was assumed, the surface Raman signal from the HNO_3 -roughened silver foil without any thermal treatment was approximately 6 orders of magnitude greater than that in solution. As for the Raman signal shown in Figure 1A, the EF was calculated to be 3.5×10^5 . Considering that the SERS effect is very sensitive to macroscopic (scale of $50\text{--}5000\text{ \AA}$) but insensitive to microscopic (atomic) surface roughness, the change in enhancement can be understood with ease. It was reported that annealing a thick silver film on a quartz substrate at $280\text{ }^\circ\text{C}$ or above, followed by the reduction of the Raman scattering signal intensity by a factor of 1, would change the macroscopic surface roughness (14). Therefore, our observation implies that the HNO_3 -roughened silver foil may be used at least under the temperature of $130\text{ }^\circ\text{C}$.

It's noteworthy that the SERS effect has almost been destroyed on the vacuum-deposited Ag/CaF_2 substrate upon heating. This result illustrates that the surface morphological structure was completely destroyed when the CaF_2 -roughened Ag substrate was heated at $130\text{ }^\circ\text{C}$. Since the silver layer only replicates the undulating structure of the CaF_2 -roughening layer onto which the metal is evaporated, such a loosely packed surface structure is readily turned into an unenhancing morphology upon heating.

We have compared Raman signals from MBI on the etched Ag substrate with those on the Ag/CaF_2 substrate. When the HNO_3 -etched Ag foil was immersed in a 10^{-3} M ethanolic MBI solution for several seconds and dried at $50\text{ }^\circ\text{C}$ for 5 min, the Raman signal intensity for the strongest 1286-cm^{-1} band in Figure 2A was 7-fold larger than that from the corresponding Ag/CaF_2 substrate (Figure 2B), with the drying temperature elevated and the time prolonged, the difference of Raman signal intensities between these two kinds of substrates became more obvious. In Figure 3B, many nonmajor peaks can hardly

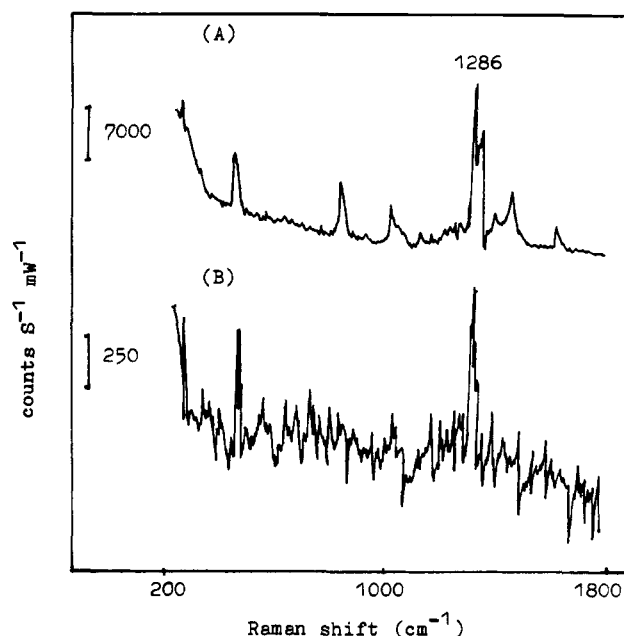


Figure 3. SERS spectra of 2-mercaptobenzimidazole (MBI) on silver substrate that was heated at $130\text{ }^\circ\text{C}$ for 12 h after sample doping: (A) on a HNO_3 -etched Ag foil; (B) on a vacuum-deposited Ag/CaF_2 substrate.

be identified, and the enhancement was almost lost for the Ag/CaF_2 substrate. Apparently, the surface silver film roughened by CaF_2 was reorganized into an unenhancing morphology after heating at $130\text{ }^\circ\text{C}$ for 12 h. However, in the corresponding SERS spectrum for the HNO_3 -roughened silver foil (Figure 3A), the intensity for the peak centered at 1286 cm^{-1} was only reduced by half, as compared with Figure 2A. Such a result may satisfy Raman spectroscopic characterization for mechanistic studies of quite a few surface reactions.

2. 4-Aminophenyl Disulfide (APDS): Solvent Resistance Studies. A surface concentration of 1.2×10^{14} molecules/ cm^2 for APDS was obtained by casting $10\text{ }\mu\text{L}$ of a $2.0 \times 10^{-5}\text{ M}$ bulk solution onto a 1-cm^2 roughened silver foil. This coverage was approximately one monolayer (12). Figure 4B shows that this adsorbate retained a narrowly stable enhancement after the Ag/CaF_2 substrate had been exposed in air for 1 h. Figure 4A is a SERS spectrum obtained from the HNO_3 -roughened silver foil. Notice that the vacuum-deposited film substrate and the HNO_3 -roughened foil spectrum are essentially identical, both in the band positions that appear and in their relative intensity. But the SERS spectrum for the HNO_3 -roughened silver foil exhibits a higher signal to noise ratio under the same condition. We find that the EF for the HNO_3 -roughened Ag foil is about 20 times greater than that for the Ag/CaF_2 substrate.

Figure 5B shows that the Raman signal intensities were reduced by more than half after the Ag/CaF_2 substrate had been heated in boiling N,N' -dimethylformamide ($\sim 153\text{ }^\circ\text{C}$) for 10 min, as compared with Figure 4B. In contrast, the Raman signal intensities for the HNO_3 -roughened Ag foil were maintained at their original values after the sample substrate had been boiled in DMF for 30 min, as shown in Figure 5A. Neither was the SN ratio in Figure 5A reduced. Again, we find that the EF for the HNO_3 -roughened Ag foil was 50 times larger than that for the Ag/CaF_2 substrate. The implications here are that the SERS effect on the HNO_3 -roughened silver foil can hardly be interfered with by the presence of an organic solvent.

Ag/CaF_2 is unstable in H_2O . When the Ag/CaF_2 substrate was heated in water for 5 min, the probe molecule almost lost its enhancement in Raman cross section (see Figure 6B).

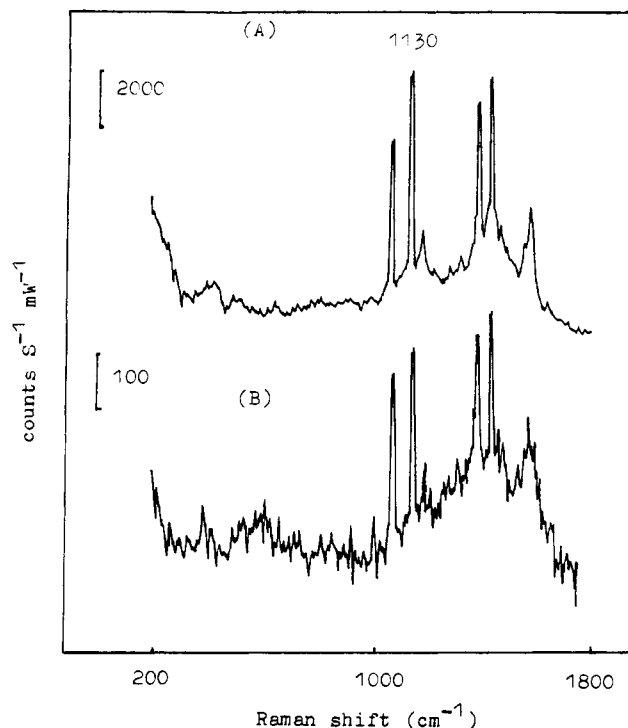


Figure 4. SERS spectra of 4-aminophenyl disulfide (A) on a HNO_3 -etched Ag foil and (B) on a vacuum-deposited Ag/CaF_2 substrate. The samples were doped on the substrates after they had been exposed to air for 1 h.

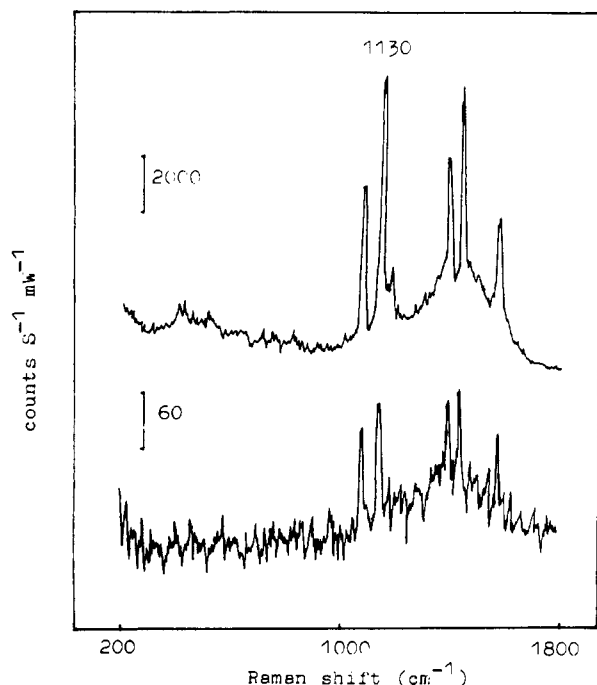


Figure 5. SERS spectra of 4-aminophenyl disulfide (A, top) on a HNO_3 -etched Ag foil that was heated in boiling DMF for 30 min after sample doping and (B, bottom) on a vacuum-deposited Ag/CaF_2 substrate that was heated in boiling DMF for 10 min after sample doping.

Nevertheless, the adsorbate continued to exhibit its reasonable enhancement on the HNO_3 -roughened silver foil, which had been rinsed in boiling water for 5 min (Figure 6A). The Raman signal intensity for the ring mode at 1130 cm^{-1} was almost maintained at the value shown in Figure 4A. The strong S-S stretching band, present in an ethanolic solution spectrum of APDS but absent in all the SERS spectra reported here, was also attributed to the facile cleavage of the

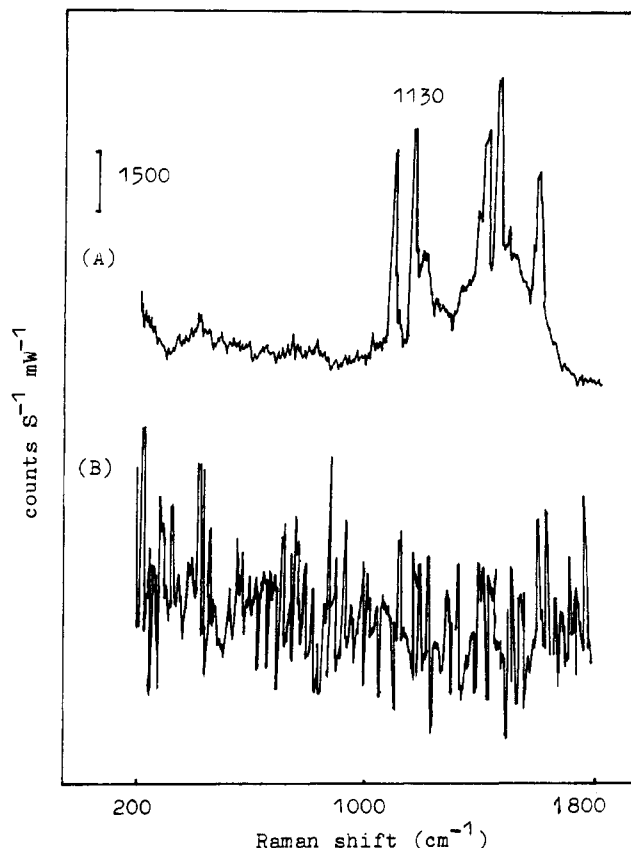


Figure 6. SERS spectra of 4-aminophenyl disulfide (A) on a HNO_3 -etched Ag foil that was heated in boiling water for 5 min after sample doping and (B) on a vacuum-deposited Ag/CaF_2 substrate that was heated in boiling water for 5 min after sample doping.

S-S bond, according to ref 14.

Since a lot of chemical reactions occur in aqueous media, the HNO_3 -roughened silver foil seems to be the most promising substrate system for Raman studies in aqueous solutions, as well as in organic solutions.

It must be pointed out that in our research phase we have also compared the thermal stability of HNO_3 -roughened SERS-active silver foils with that of copper foils. The results show that oxide overlayers are frequently formed on copper foils when some corrosive compounds are adsorbed at elevated temperatures, since copper is easier to oxidize than silver. And it has been found that oxide formation on etched copper foils prior to SERS measurements will reduce the EF by a factor of at least 1. The trouble may be overcome when a HNO_3 -etched silver foil is used as the analytical tool for routinely preparing substrate systems for SERS studies.

CONCLUSIONS

In this paper we have evaluated the use and performance of a simple and inexpensive silver substrate system for Raman studies, which could significantly increase the applicability of the SERS techniques. We have also performed SERS measurements with this substrate system on molecules of current interest. The results show that a number of sulfur-containing compounds adsorbed on variously conditioned surfaces can easily be detected by the SERS technique using solid silver media etched by concentrated HNO_3 . The results of this work also show that our SERS sampling technique is particularly efficient. The feature is of great importance, since practically applicable conditions are commonly found in various solvent media and at elevated temperatures with prolonged times. The future work will certainly be attractive in the field concerned although this is merely a first report on developing tentatively the technique as an analytical tool

for the characterization of chemisorbed species on silver under different environmental conditions.

Registry No. Ag, 7440-22-4; HNO₃, 7697-37-2.

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Preparation of Phosphate Samples for Oxygen Isotope Analysis

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The potential of oxygen isotopic analysis on natural phosphates has long been known but has not been fully realized for want of a simple analytical technique. For example, paleotemperature measurements based on ¹⁸O/¹⁶O ratios of fossil carbonates are well established (1). In principle, the corresponding phosphate paleothermometer should be more stable and resistant to alteration in the sedimentary environment because a phosphate ion in a crystalline lattice exchanges oxygen isotopes with water more slowly than carbonate ion. This phosphate paleothermometer, however, is not nearly as well developed and exploited as the one based on carbonate primarily because of the relative difficulty of the phosphate preparation technique (2).

A method for the ^δ¹⁸O isotopic analysis of phosphate was presented by Tudge (2). Subsequent modifications were made by Longinelli and co-workers (3-7) and by Kolodny and co-workers (8-10). In this procedure, phosphate ions are isolated as BiPO₄·H₂O after a three-stage, wet chemical separation. The product is dehydrated to α-BiPO₄, which is hygroscopic. Karhu and Epstein (11) converted the anhydrous α phase to the less hygroscopic β phase. The resulting bismuth phosphate is reacted quantitatively with bromine pentafluoride to yield O₂, that is converted to CO₂ for isotopic analysis in a ratio mass spectrometer.

The bismuth phosphate method is not optimal because (1) the preparation method is tedious multistep and time consuming, (2) a relatively large sample is required, and (3) bismuth phosphate is hygroscopic. We have simplified this procedure by using anion-exchange chromatography for isolation and purification of phosphate ions for geological matrices. Phosphate in slightly alkaline solution exists as a trivalent anion that is retained strongly on an anion-exchange resin. Mono- and divalent ions can be washed out completely without loss of phosphate. Using an eluant solution of ammonium nitrate removes the dihydrogen phosphate ion sharply in a minimum volume. Silver phosphate is then precipitated by the method of Firsching (12). Silver phosphate was chosen because it is one of the few phosphates that precipitates from

aqueous solution in a simple stoichiometry without a water of crystallization and is not hygroscopic. Baxter and Jones (13), in a classic study, determined the properties of Ag₃PO₄ and found it suitable (pure, stable, nonhygroscopic) for determining the atomic weight of phosphorus. A preliminary report on the feasibility of the silver phosphate method for isotopic analysis was published by Wright and Hoering (14) in which several problems were identified. These problems have been addressed, and the refined methodology for isotopic analysis is presented here.

EXPERIMENTAL SECTION

Materials. Chemicals used in the present work were reagent grade. The NBS 120c reference material (Florida Phosphate Rock Standard) was obtained from the National Institute of Science and Technology, Gaithersburg, MD. The Ag₃PO₄ internal laboratory reference material is Aldrich No. 33.738-2. The ion-exchange resin is Amberlite IRA-400(OH), a strongly basic gel-type resin (Aldrich Chemical Co.). High-purity bromine pentafluoride (Ozark-Mahoning Chemical Co., Tulsa, OK), containing less than 1% contaminants, was used to react the silver phosphate.

Instrumentation. All samples were digested and prepared in a dedicated room and fume hood system to avoid airborne contamination. Glassware and plastic centrifuge tubes used in this procedure were rinsed repeatedly in deionized redistilled water. All glassware was precombusted at 500 °C for 4 h in an annealing oven prior to use. Silver phosphate samples were reacted in a fluorination reaction line (Figure 1) constructed of all-nickel tubing (No. 201) silver-soldered to monel bellows valves (Nupro No. BF-4BK). Each reaction vessel was constructed of solid nickel stock and connected to a monel bellow valve by a welded solid nickel VCR fitting. The entire reaction line had a total volume, including the reaction vessel, of less than 0.2 L. The fluorination reaction line was totally dedicated to silver phosphate and non-ferrous silicate minerals (reaction of ultramafic minerals in fluorination lines has been related to slight positive isotopic deviations). Vacuum on the fluorination side of the line was provided by an oil-free, molecular sieve, cryogenic pump (10⁻⁴ Torr; Vacorb by Varion No. 941-6501). Released oxygen gas was purified through two nickel U-traps immersed in liquid nitrogen and converted to CO₂ in a 600 °C platinum-catalyzed graphite O₂/CO₂ conversion furnace. The CO₂ was passed through a silver wool furnace at 650 °C to remove any halogen gas. Vacuum on the borosilicate/quartz glass side of the line used for O₂/CO₂

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