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Isotopic hydrogen analysis via conventional and surface-enhanced fiber optic Raman spectroscopy

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ABSTRACT

This report describes laboratory development and process plant applications of Raman spectroscopy for detection of hydrogen isotopes in the Tritium Facilities at the Savannah River Site (SRS), a U.S. Department of Energy complex. Raman spectroscopy provides a lower-cost, *in situ* alternative to mass spectrometry techniques currently employed at SRS. Using conventional Raman and fiber optics, we have measured, in the production facility glove boxes, process mixtures of protium and deuterium at various compositions and total pressures ranging from 1000 – 4000 torr, with detection limits ranging from 1-2% for as low as 3-second integration times. We are currently investigating fabrication techniques for SERS surfaces in order to measure trace (0.01-0.1%) amounts of one isotope in the presence of the other. These efforts have concentrated on surfaces containing palladium, which promotes hydrogen dissociation and forms metal hydride bonds, essentially providing a chemical enhancement mechanism.

Keywords: Process analysis, fiber optic probes

1. INTRODUCTION

The Savannah River Site (SRS) in Aiken, SC, performs production scale separation and purification of tritium. This work includes the separation of tritium from other hydrogen isotopes using the Thermal Cycling Absorption Process (TCAP).[1-3] TCAP is a cryogenic process which achieves separation through the differential absorption of isotopes onto a catalytic column. A schematic describing the process is shown in Figure 1. An initial concentration profile on the separation column is generated by loading gas from the plug-flow reverser (PFR) to the cooled bed. When column capacity is reached, the column is heated and the gas is allowed to flow, without mixing, back into the PFR. Repeated temperature cycling improves the separation. Once a steady state has been reached, semi-continuous operation is possible. Gas is withdrawn at the product and raffinate (waste) ends during the hot part of the cycle and loaded from a feed bed at the column midpoint as the column is cooling. The temperature cycle is then repeated to re-establish the concentration gradient.

Proper TCAP operation requires that the hydrogen inventory withdrawn during the hot cycle be matched by the feed supplied during the cold cycle. Assuring this match requires accurate measurement of the isotopic composition and the total amount of gas withdrawn and fed. The latter are made by standard pressure measurements in a calibrated volume (CV). At SRS, isotopic measurements have historically been made by at-line mass spectrometry (MS). While MS has been adequate, there are several reasons to pursue alternative measurement strategies. For example, the mass spectrometers are too large to fit in the glove box used to contain the TCAP, therefore requiring gas delivery through a capillary line. There is a delay associated with gas transport as well as an increased possibility of system leaks. Also, instruments with the required resolution are very expensive. There is a maintenance issue associated with the particular spectrometers being used at SRS, as the original vendor has stopped supporting those instruments. Therefore, recent development work at SRS has included an examination of possible replacement analysis systems.[4-5]

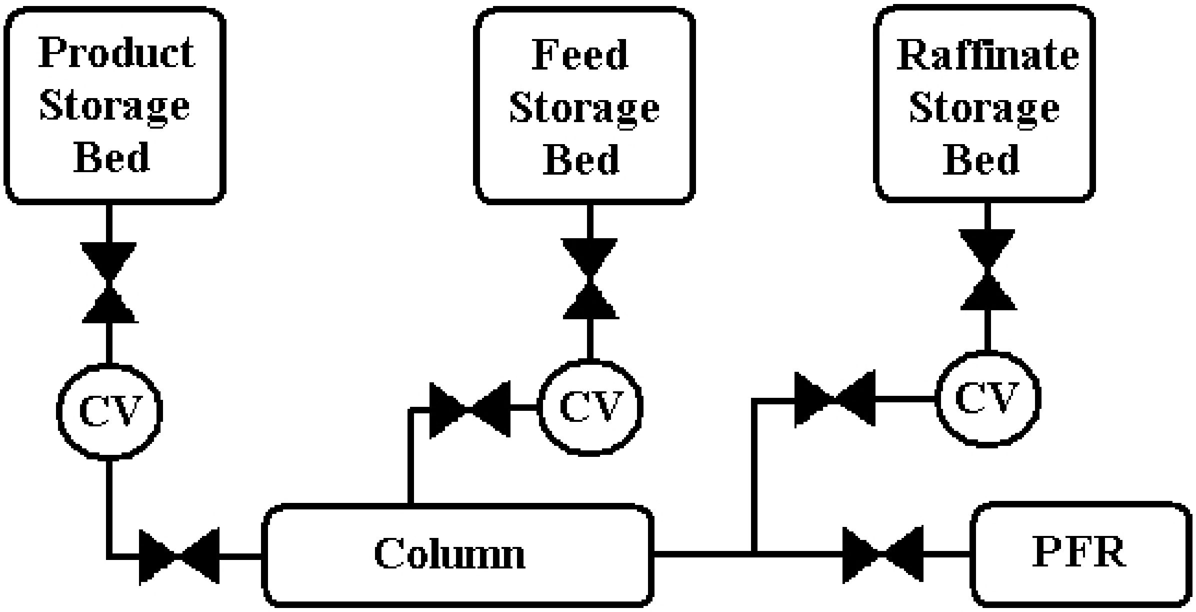

Figure 1. Schematic of the TCAP process.

One measurement alternative is Raman spectroscopy. Isotopic identification is easy for hydrogen due to the large vibrational energy differences between species.* The large shifts also allow a simplified probe design, as the analyte peaks are well removed from the strong silica fiber Raman bands. Fiber optic probes simplify the interface with the gas manifold and glove box, which is attractive for a process where containment of a radioactive gas is a primary concern. They also promote safety, as most workers will not have laser training. Analyses can be made more quickly and at lower cost than with MS.

As with most Raman applications, the primary problem is sensitivity, as illustrated by the TCAP measurement requirements. There are three measurement points– the feed, the product, and the raffinate. The feed requirements are the easiest to meet, with the smallest fractional concentrations near 1%, total pressures 2000-4000 torr, temperatures near 130 ^{o}C, and with up to 1 minute available to make the measurement as the gas is sorbed onto the column. Assessing the purity of the product and raffinate, however, requires much more sensitivity – approximately 0.1% of the lighter isotope for the product, and 5-10 ppm of the heavier isotope for the raffinate. Feed measurements are within the scope of "conventional" Raman spectroscopy and fiber probe technology, but the product and raffinate measurements require significant improvements or enhancements.

We have therefore started to develop surface-enhanced Raman spectroscopy (SERS) materials and methods to improve our sensitivity[7]. The idea of applying SERS to vapor-phase species has been considered for many years. Target analytes are typically explosives[8] or volatile organics, including conjugated ring structures and organohalogens.[9-13] While SERS promises enhanced Raman scattering through electromagnetic or chemical enhancements, almost all of these reports describe the use of surface functionalization, polymer coatings, or mechanical means to concentrate the vapor at the surface. Although these techniques are useful for many applications, they are not applicable to tritium measurements in TCAP. Tritium is known to attack hydrogen-containing compounds, ruling out most functionalizations and polymers. Also, the amount of cooling required to obtain significant concentration at the SERS surface is beyond the capacity of any device that will realistically be installed in the glove box. A different approach is required.

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[*] Q branch, $J = 0$ peak positions, except as noted: H_2: 4155 cm^{-1}; HD: 3632 cm^{-1}; HT: 3435 cm^{-1}; D_2: 2994 cm^{-1}; DT: 2738 cm^{-1} ($J = 2$); T_2: 2461 cm^{-1} ($J = 2$).[6]

2. EXPERIMENTAL

Figure 2 shows the laser and probe interface used for both development work and field demonstrations. The laser is a Sapphire 200-488 200-mW CW diode laser emitting at 488 nm (Coherent, Santa Clara, CA). All of the laser components (head, heat sink, control board, and power supply) are packaged into a 12” x 13.5” x 8.5” portable system. A computer is used to control the laser through a RS-232 connection. Laser output is coupled into the fiber probe through a 0.22 numerical aperture (NA) collimator (World Precision Instruments, Sarasota, FL). Tests show 85% light transmission at the end of the probe, near the maximum expected for four air/glass interfaces.

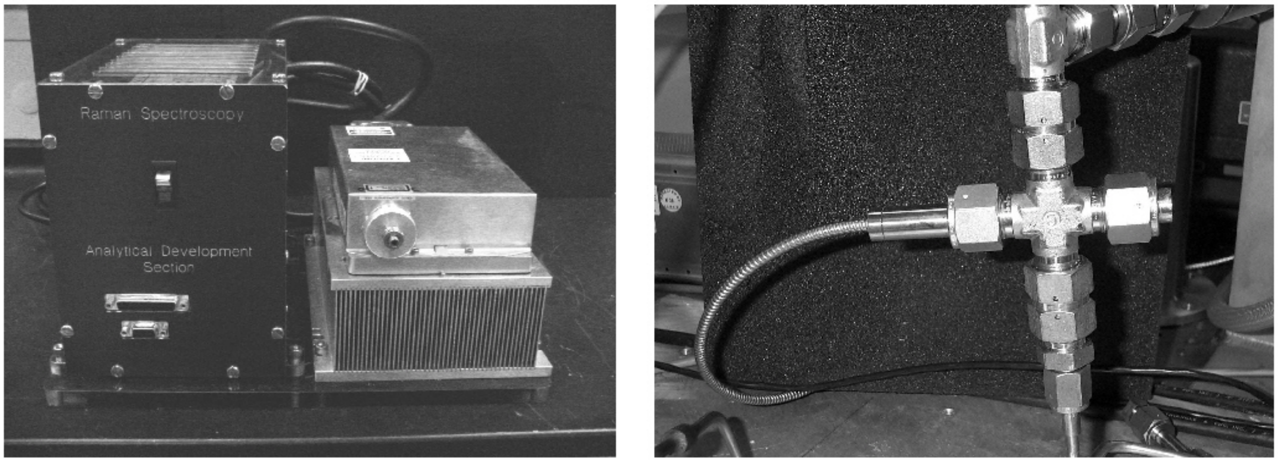

Figure 2. Repackaged laser (left) and fiber optic probe interface (right).

The fiber probe (RoMack, Williamsburg, VA) is 20 feet long and employs a standard 6-around-1 configuration with the collection fibers surrounding the excitation fiber. All fibers are 400 micron diameter with a 0.22 NA. The common end is a ½-inch VCR fitting, and both instrument ends have SMA fittings. All fibers are enclosed in stainless steel jacketing. In field demonstrations, the fiber penetrates the TCAP glove box through a glove port cover. The fitting is made by removing a small section of the steel outer jacket and teflon inner fiber jacket and potting the exposed fibers in epoxy (Douglas Electrical Components, Rockaway, NJ). The fiber lengths are continuous; there is no break for a bulkhead connection, for example. The probe is fit to a port in a VCR tee at various positions near the column midpoint.

Spectra are collected with a Holospec f/1.8 I VIS spectrometer (Kaiser Optical Systems, Ann Arbor, MI), with a 488 nm SuperNotch-Plus filter to reject Rayleigh scattering and a 1024 x 256 CCD detector array (Andor Technology, South Windsor, CT). Data are generally acquired using 5- or 15-second integration times and 5x averaging for lab work, and with 3-5 second integrations for field work.

The results reported here do not include any tritium data. For laboratory work, mixtures of H_2 and D_2 were made in-house at various compositions (nominally 95:5, 74:26, 50:50, and 25:75) from commercially available sources (Scott Specialty, Wakefield, MA). The composition of gas mixtures measured in the field was confirmed by residual gas analysis (RGA) and MS of gas collected in sample bombs. Laboratory measurements were taken at room temperature. Field measurements were taken at TCAP process temperatures (room temperature up to 130 ^{o}C).

Metallic thin-film surfaces for SERS measurements were fabricated by a variety of methods. Ag and Pd/Ag films were deposited on 10 mm diameter curved and flat optical blanks (Edmund Scientific, Barrington, NJ) by vacuum ion deposition. Typical deposition rates were 2 Å/s. Sol-gel encapuslated Ag particles were fabricated after the method of Dai.[14] Pd and Ag colloidal solutions were made by laser ablation of submerged metallic rods, as described by Cotton.[15] Colloids were later deposited onto metal rods by electrolysis. Nanopatterned Ag- and Ag/Pd-island surfaces were fabricated after the method of van Duyne.[16] All materials except the colloids were investigated for hydrogen and nitrogen SERS activity by placing them in front of the probe described above. The samples were positioned face-on or at a 45-degree angle using custom-machined holders that fit into the opposite side of a VCR cross from the probe. The colloids were tested by bubbling H_2 through the colloid solution, and measuring Raman scattering from the liquid.

Supporting calculations were carried out with Matlab, version 6.0 (Mathworks, Natick, MA).

3. RESULTS AND DISCUSSION

3.1 Conventional Raman Measurements

The use of Raman spectroscopy for hydrogen isotope identification and detection in nuclear processing applications has been considered for many years. These efforts evolved from off-line analysis of collected gas[17] to at-line measurements using specialized gas cells and free-beam lasers[18,19], with subsequent use of fiber optics with external gas cells.[20-22] None of these approaches met one or more of the requirements for TCAP implementation, specifically contained laser energy, ease of use, a rugged on-line sampling interface, and minimal use of glove box space. Several, particularly those which incorporate pressurized gas cells or free-space beams, also make it difficult or expensive to use a single instrument to measure multiple process points.

These issues can be addressed with the use of a single fiber optic probe for both excitation and collection of scattering. These probes are widely used for liquid and solid samples[23] but have found much less application for gas analysis. Berg and co-workers have described some practical considerations of using these probes.[24] They examined the effect of probe (angle and numerical aperture of fibers, use of windows and internal filters) and sample chamber design on collected Raman and background scattering. They found that non-imaging, unfiltered probes achieve lower detection limits than filtered, imaging probes as long as the sample chamber does not lead to excess scattering and that a protective window is not incorporated into the probe tip. We have followed a similar approach by using an unfiltered, 6-around-1 (non-imaging) probe without a protective window, and where possible used a black-anodized, curved metal surface as a beam stop.

Several typical laboratory spectra of H_2 (4155 cm^{-1}) and D_2 (2994 cm^{-1}) at different ratios are shown in Figure 3. They are corrected for background silica scattering by subtracting a blank spectrum taken in a vacuum. Background levels were consistent over a period of at least several hours. The background's consistently smooth shape suggests that polynomial modeling techniques[25] could be used to correct for it automatically, though these techniques were not implemented in this work. In some spectra, the formation of HD (3632 cm^{-1}) is evident. Also observable are several ro-vibrational lines for H_2, which has the largest line spacing of the different isotopes. Because most of the intensity for each isotope appears in one peak, and as the higher rotational lines would be difficult to measure for low concentrations of H_2, we determine concentrations by measuring the peak height of the primary peak. Peak area calculations yield similar results. We also assume that the Raman scattering cross-section of the different species are identical, which is accurate within a few percent.[26]

The observed scattering was proportionally consistent over a wide range of isotopic ratios and total pressures. Figure 4 shows the linear response for nominal H_2/D_2 ratios of 75:25, 50:50, and 24:76, measured from several thousand Torr. Linearity is also seen through the consistent H_2/D_2 ratios demonstrated in Figure 5. While the uncertainty of the isotopic ratio increases as the overall signal declines, the ratio is consistent over a large pressure range, indicating the system's utility.

The estimated limit of detection (LOD) of both H_2 and D_2, shown in Table 1, is also consistent. The LOD is calculated as the partial pressure of gas that gives rise to a signal three times the standard deviation of the baseline noise. Relative to the measurement conditions of the process (~3000 Torr), the observed LOD indicate a potential detection limit of 0.2-0.4% at higher pressures, which is adequate for the TCAP column midpoint.

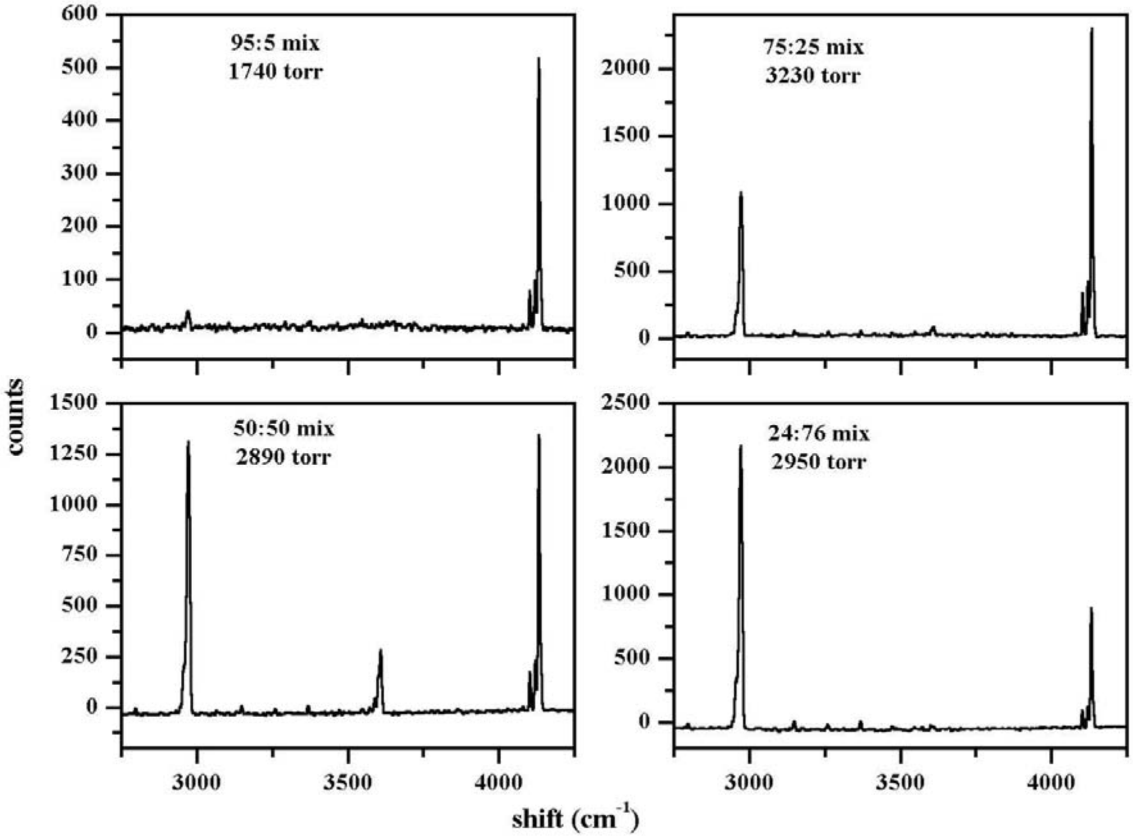

Figure 3. Observed spectra for a variety of H_2/D_2 ratios. Spectra were obtained with 15 second integration times.

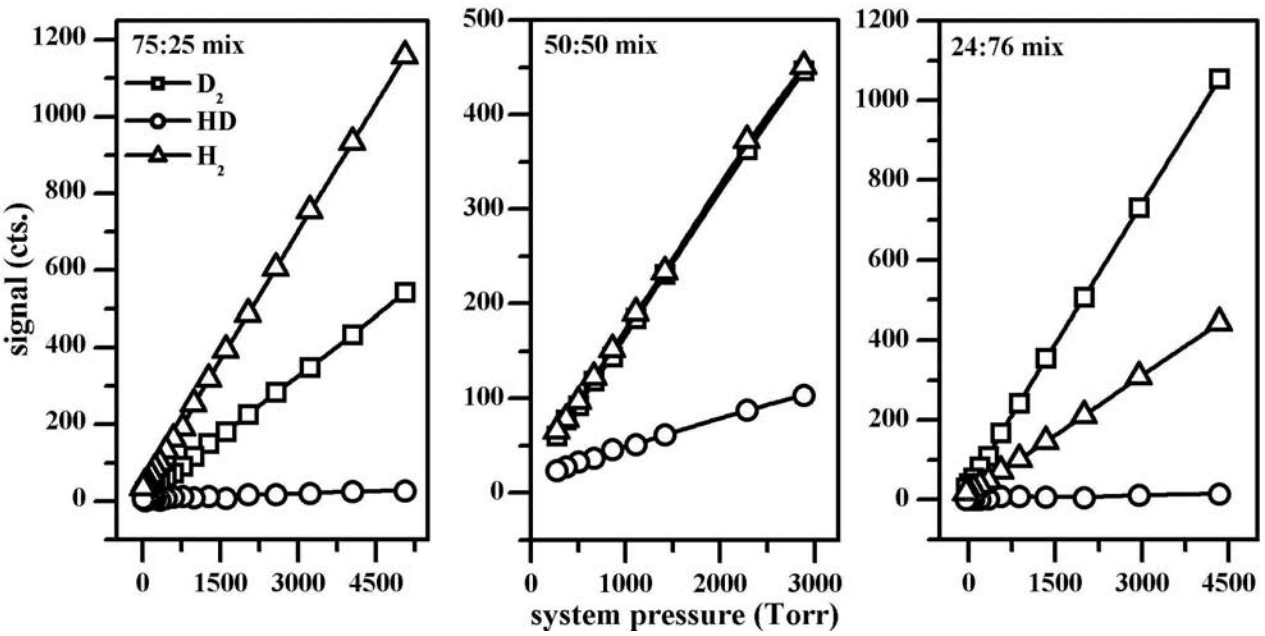

Figure 4. Dependence of peak height on system pressure for H_2:D_2 mixes.

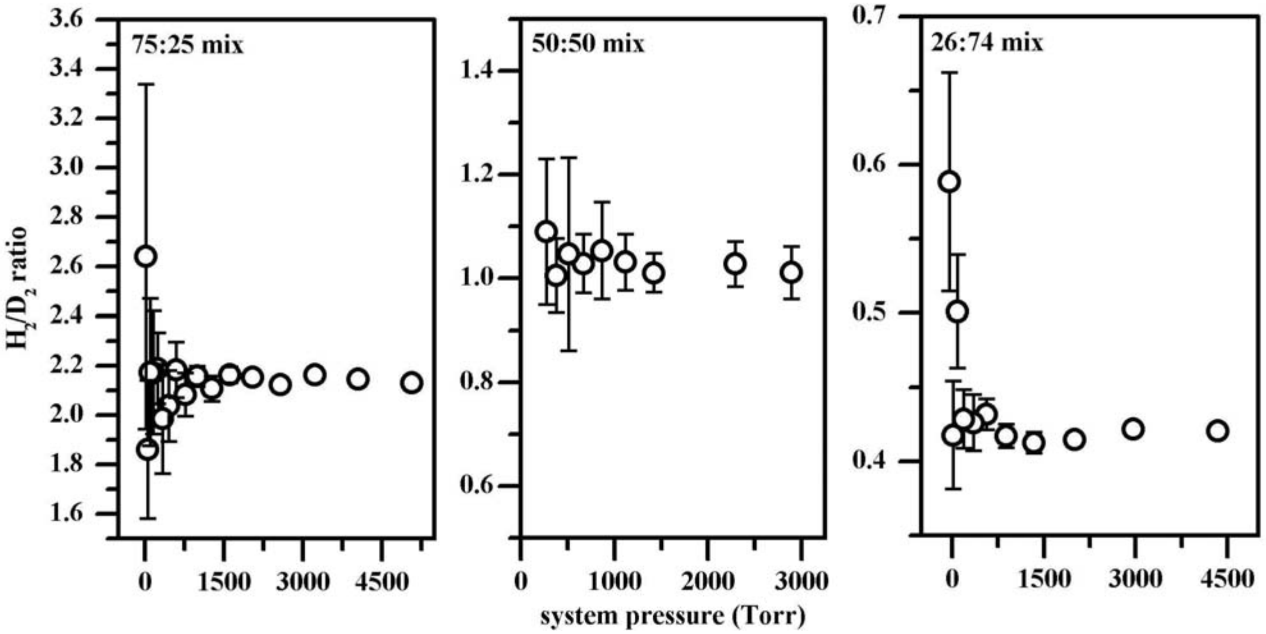

Figure 5. Dependence of measured isotopic ratio on system pressure.

Table 1. Estimated limits of detection (LOD) for H_2 and D_2 for different mix ratios and system pressures.

H_2:D_2 ratio	P_{TOTAL} (torr)	H_2 LOD (torr)	D_2 LOD (torr)
25:75	593	4.3	5.6

	3229	4.9	6.0
50:50	189	4.8	5.5
	2886	8.1	8.5
75:25	562	9.7	7.2
	2953	7.3	6.6
95:5	394	4.6	5.4
	1740	6.6	10.4
	Average ± 1σ	**6.3 ± 2.0**	**6.9 ± 1.8**

It is also interesting to compare the system LOD with other reported work involving similar equipment. These comparisons are complicated by the variation in experimental conditions. Laser power and wavelength, accumulation time (integration time multiplied by the number of averages), and laser power all affect the signal-to-noise ratio. To reduce this variation, one may define a Raman figure of merit (FOM),

$$\mathrm{FOM} = \mathrm{LOD}\ (\mathrm{torr}) \cdot t\ (\mathrm{sec}) \cdot \mathrm{P}\ (\mathrm{mW}) \cdot R\ , \tag{1}$$

where t is the accumulation time, P is the laser power, and R is a factor capturing the wavelength dependence of Raman scattering (= $(488/\lambda)^4$, where λ is the excitation wavelength in nm, and the excitation wavelength of this work, 488 nm, is chosen as an arbitrary reference). The FOM is defined such that a lower number represents a more sensitive system. Table 2 shows results for our system and several others. As calculated, our FOM is competitive with the other values reported. The comparison with the values of O'Hira[20] and Nave[22] indicates that unusual collection methods (e.g. a multipass gas cell or a pressurizing collection chamber) are not necessary to obtain low detection limits. As the equipment used by Berg[24] was similar to ours, it is likely that the differences arise from their emphasis on characterizing background noise rather than increasing Raman scattering.

Table 2. Comparison of methods for fiber optic Raman detection of hydrogen.

Reference	**LOD (Torr)**	**Parameters**[a]	**FOM**[b]	**Comments**
[20]	2	100 s, 700 mW, 488 nm	1.4×10^5	Separate collection and excitation probes Glass Raman cell
[22]	15	20 s, 400 mW, 488 nm	1.2×10^5	Pressurized gas cell Filtered 6-around-1 probe Angled collection fibers
[24]	0.5	1200 s, 430 mW, 532 nm	1.8×10^5	Unfiltered 9-around-1 probe
this work	7	75 s, 170 mW, 488 nm	0.9×10^5	Unfiltered 6-around-1 probe

[a] Acquisition time (integration times averages), laser power, laser wavelength. [b] Defined in Equation 1.

In passing, we note a brief experiment in which the beam block is replaced with a spherical mirror positioned with excitation fiber at its focus. As the front end of the probe is made of smooth stainless steel, this forms a crude multipass chamber that is compatible with being used in a VCR fitting. This arrangement leads to a 2.5-fold increase in peak height for H_2. The increase is (unsurprisingly) accompanied by a 250-fold increase in background levels due to the improved collection efficiency for Rayleigh scattering, making the spectra difficult to interpret. Still, this result suggests that some kind of multipass arrangement could be incorporated into a probe based on a VCR fitting, perhaps with the incorporation of holographic filters to remove fiber scattering.

Field demonstrations gave similar results to those obtained in the laboratory, despite unique conditions presented for each TCAP run. For example, during measurements of the 50:50 H_2/D_2 mix the probe collected room light through the plastic capillary used for concurrent RGA measurements. Unlike the laboratory samples, TCAP gases had rapid isotopic equilibration due to dissociative absorption on the column. Accordingly, the H_2/D_2 ratio was calculated by adding half the HD peak height to the H_2 and D_2 heights. Despite the added uncertainty associated with incorporating a third measurement to the ratio, the results agreed within 2-5% with RGA and MS measurements. Demonstrated LODs correlate to 1-2% for short integration times, which is adequate for TCAP measurement.

Other advantages of Raman measurements were evident from the demonstrations. Figure 6 shows the ability of the technique to monitor column kinetics in real time, taken in this case for a 40:60 mix. Here, the differential affinity of H and D for the column is shown by a series of spectra taken while the column is heated. At the beginning of the cold cycle, there is more deuterium than hydrogen evolving, but the ratio changes as the column is heated. These spectra were acquired with three second integration times and could be analyzed nearly instantaneously. Such real-time feedback is not possible with MS or RGA due to the lag time associated with transporting gas through capillary tubes.

Other demonstrated advantages of Raman analysis are its speed and simplicity. Measurements can be taken in a few seconds, compared to several minutes for RGA. Spectral acquisition can be reduced to a few mouse clicks. There are no process lines that need flushing between measurements. The rations are not sensitive to system pressure, as they are RGA. The Raman spectrometer became the instrument of choice for TCAP engineers during startup troubleshooting work.

3.2 Surface-Enhanced Raman Spectroscopy

The 1-2% detection limits shown for column midpoint measurements with the conventional Raman probe are 1-2 orders of magnitude too high for product purity measurements. Raffinate measurement requirements are more stringent, reflecting limits for environmental release. SERS offers the hope of improved detection limits using process-compatible materials. Our work has concentrated on bare metal surfaces, which would be expected to be more stable in a hydrogen environment. We considered several different routes to making SERS surfaces, including vapor phase deposition, incorporation of nanoparticles into a sol-gel, colloid formation (with subsequent electroplating onto a substrate), and nanolithography. We chose this variety of techniques in part to investigate which might prove to be the most reliable method. Some techniques were also chosen to leverage techniques learned from other projects. We made the surfaces while trying both to maintain compatibility with equipment used for the conventional Raman measurements and to minimize the potential impact on TCAP. This approch has the best chance of retaining a high degree of confidence from process engineers. Therefore, design considerations included using a substrate that could be mounted opposite the probe and illuminated. Also, we restricted material choices to Ag or Pd/Ag alloys that would be expected to have plasmon resonances near 488 nm.

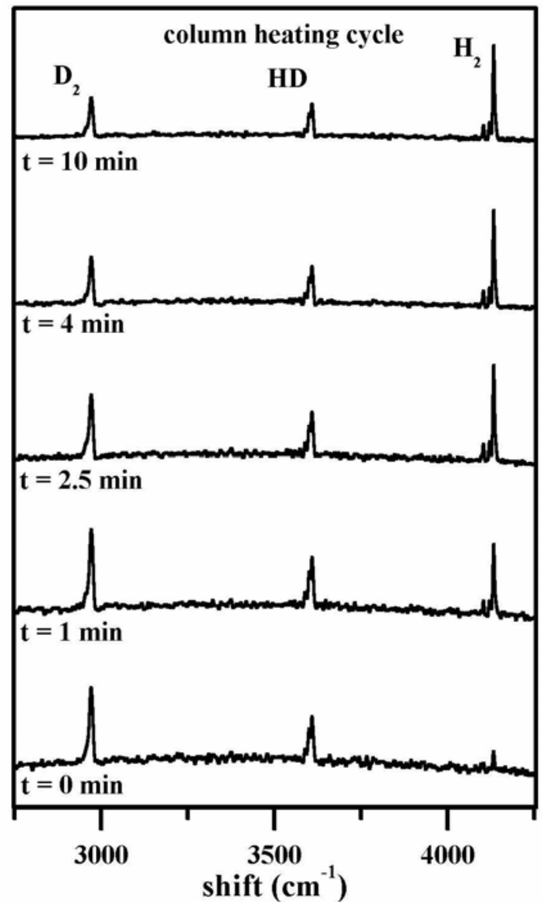

Figure 6. Time evolution of hydrogen absorption from TCAP column.

Unfortunately, all of the materials tested to date have the common feature of not providing any observable SERS enhancements for hydrogen. We expected to see either greater scattering at 4155 cm^{-1} for purely electromagnetic enhancement with no H_2 dissociation, or a peak near 2000 cm^{-1} representing the formation of a Pd-H bond.[27] Efforts are continuing to improve the SERS materials and experimental arrangement. Even with expected improvements, there are several factors worth noting which may make effective SERS enhancement difficult.

Volumetric considerations. Because the light exiting the probe is unfocused, the effective volume sampled is relatively large compared to focusing probes. The spatial dependence of the collected Raman signal can be calculated from the probe geometry (fiber diameter, separation, and angle) and fiber numerical apertures.[28] Figure 7 shows the dependence of the collected scattering on the distance z from the face. The low intensity at small z is defined by the numerical aperture of the fibers, while the decrease at larger z is determined by the reduced solid angle. These results indicate that there is substantial Raman scattering collected up to 10-15 mm away from the fiber face.

The curve also indicates an optimal position to place a SERS surface to maximize collection efficiency using the same probe: z = 3600 μm in this case. In this arrangement, the total Raman signal collected will be the sum of the conventional Raman scattering from the volume above the surface plus the SERS scattering close to the surface. Thus, an increased Raman signal will only be observed if the SERS signal is greater than the excluded free-space Raman signal (i.e. behind the surface). One can estimate the effective electromagnetic scattering volume as twice the mean diameter of the surface roughness features,[29] or roughly 100 nm. For a surface placed at z = 3600 μm, the predicted conventional

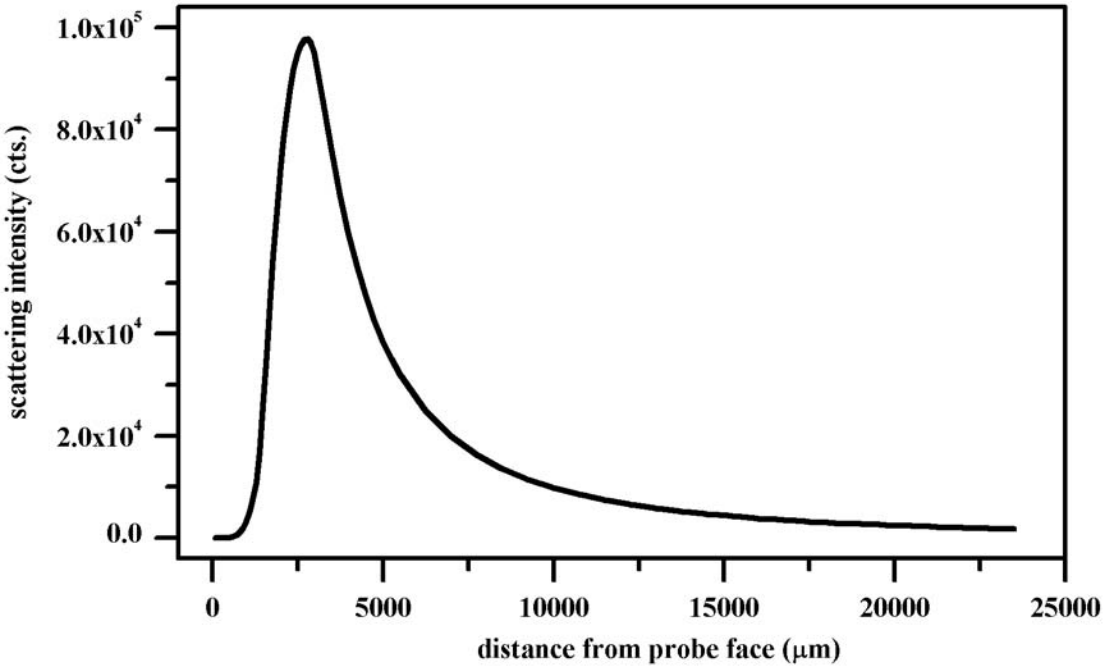

Figure 7. Dependence of collected Raman intensity on distance from the probe face, for 6-around-1 probe with 400 μm fibers, separated by 500 μm.

Raman scattering from the SERS-active volume element is 1.0 x 10^4 (using the units of Figure 7). In comparison, the intensity from the excluded volume is 3 x 10^8. Thus, enhancement factors of 3 x 10^4 are required to see any enhanced signal. This calculation in fact underestimates the total enhancement required, as the SERS signal will decrease exponentially from the surface, and thus the effective volume which must be considered is smaller than 100 nm. While the required enhancement is not unrealistic, it does indicate that careful consideration must be made to optimizing all experimental parameters, including surface quality, matching the excitation wavelength to the surface optical properties, and choosing the right surface mounting distance.

Materials considerations. Silver SERS surfaces were initially chosen because their typical resonance wavelengths more closely match the 488 nm excitation wavelength. However, there is very little interaction between Ag and hydrogen that would cause hydrogen to adsorb onto the surface.[30] Consequently, any SERS enhancement for a silver surface will likely come from electromagnetic contributions, not charge transfer (CT). Pd surfaces, either alloyed with Ag[30] or as a thin (few monolayer) cap,[31] should permit hydrogen concentration at the surface, facilitating CT enhancements and increasing number density, without significantly changing the SERS properties. Because the surface will be alternately exposed to high and low hydrogen pressures, it will have to retain its structure after many cyclings. A recent report[32] suggests that Ag nanowires coated with Ag/Pd alloy sheaths withstand the lattice deformation associated with H adsorption much better than pure Pd nanowires.

Some probe redesign may also be in order if Pd-containing surfaces are used. The Pd-H vibration at approximately 2000 cm^{-1} does not overlap silica fiber bands, but the Pd-D and Pd-T vibrations at lower frequencies do. While we have had success routinely subtracting the fiber background from our spectra, we must be concerned about detector saturation if excessive integration times or laser powers are used. Effective use of the Pd-hydrogen peaks may require a new probe design that includes a bandpass filter to remove fiber scatter.

4. CONCLUSION

This work demonstrates the feasibility of using fiber optic-based Raman spectroscopy for *in situ* hydrogen isotope analysis in support of tritium processing operations at SRS. The sensitivity of laboratory based measurements is competitive with others reported in the literature. Rapid and accurate spectral acquisition during field trials permits the use of the system for process troubleshooting. The simplicity of the equipment and its operation means that it is suitable for permanent installation into the process.

However, several improvements are required to fully realize the technique's potential. The system will be most effective if it can monitor multiple points. For TCAP, that means improvements of 1-2 orders of magnitude through probe design and/or SERS surfaces to facilitate trace analysis of the product stream, and an additional 1-2 orders improvement for the raffinate stream. Improved probe design can be realized through optical filters, multipass arrangements, optimization of fiber placement and properties. Preliminary work with SERS surfaces has failed to generate significant enhancements. Continued work with Pd/Ag alloys and caps may provide the required improvement.

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