A Clinical Probe Utilizing Surface Enhanced Raman Scattering

*J. Kim, D. Hah, T. Daniels-Race, and M. Feldman**
Division of Electrical and Computer Engineering
Louisiana State University, Baton Rouge LA, 70803-5901
E-mail: mfeldm1@lsu.edu

Raman spectra have been used to identify substances for many years. The generally weak Raman signal levels are enormously enhanced when the specimen are in contact with a rough metallic surface. There is considerable interest in extending this Surface Enhanced Raman (SER) capability to an endoscopic probe, so that samples may be studied *in vivo*, rather than removed and placed on a microscope stage. In previous work[1] the authors obtained SER spectra through a rough gold film on a transparent substrate, so that access was needed to only one side of the sample (Fig. 1). In the present work a graded index (GRIN) lens, permanently attached to the rough gold film, replaces the Raman spectrometer's microscope objective (Fig. 2). The 2 mm diameter of the GRIN lens lends itself to incorporation in a needle like endoscopic probe, and its 0.3 NA is comparable to that of a 10X microscope objective. Figure 2 illustrates a fixed focus probe, since once the GRIN lens is focused on the gold film no further adjustment is needed. However focusing capability was included in the prototype probe, making it somewhat wider.

In clinical applications the probe must be capable of pointing in any direction at any point within a sizable working volume. This was accomplished by coupling the GRIN lens to the spectrometer with a single mode optical fiber. However the background signal from the fiber masked the Raman signal from the probe. Therefore an articulated arm was constructed (Fig. 3). With the microscope objective removed, the light exiting our Horiba LabRAM spectrometer is a slightly diverging 633 nm HeNe laser beam. The mirrors M_1 placed on the spectrometer stage, and M_2 on the arm's support base, direct the beam down the axis of the arm. The beam is brought to a waist by a single long focal length lens, and then expands to fill the GRIN lens. For clarity the arm is shown in a stretched out top view, but in practice rotation occurs at any of the right angle 45^o mirror elbows. Thus, point B may be positioned on a circle of radius L_1 centered at point A, and point C (approximately) on the surface of a sphere of radius L_2 centered at B. In principle point C may be positioned anywhere within a torus of major and minor radii L_1 and L_2, respectively. In practice $L_1 >> L_2$ and the useful working volume is approximately a circular cylinder of diameter and height $2L_2$, located a distance L_1 from the base and a further distance X from the spectrometer. The last two elbows point the GRIN lens in any direction.

Figure 4 shows the Raman spectrum obtained by pressing the probe against the surface of a gelatin sample. The gelatin was prepared normally, but with a 1 mM solution of Rhodamine 6G instead of water. To our knowledge this is the first time an SER spectrum has been obtained with access to only one side of a solid specimen. In addition the narrow probe diameter facilitates obtaining spectra within a specimen.

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1) J. Kim et. al. *J. Vac. Sci. Technol.,* vol. B-31, no. 6, Nov/Dec, 2013.

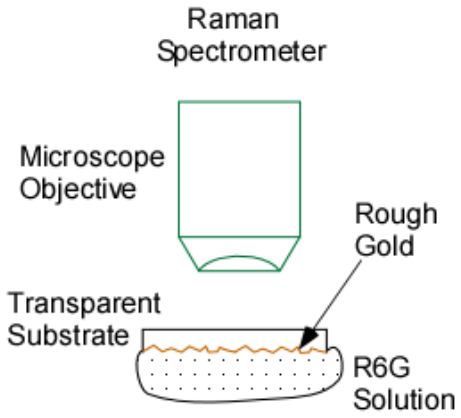

Fig. 1. Focusing through the rough gold using a microscope objective on the Raman spectrometer.

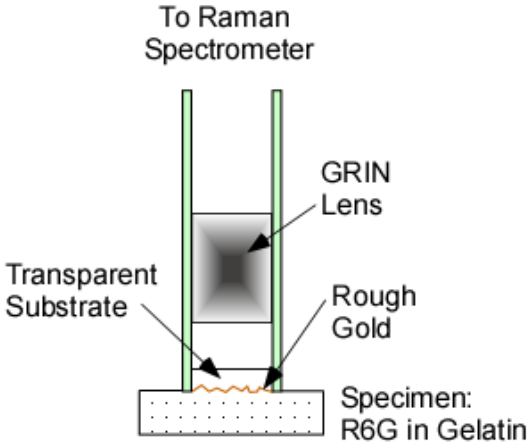

Fig. 2. Replacing the microscope objective with a GRIN lens permanently focused on the rough gold. The probe is then pressed against the specimen.

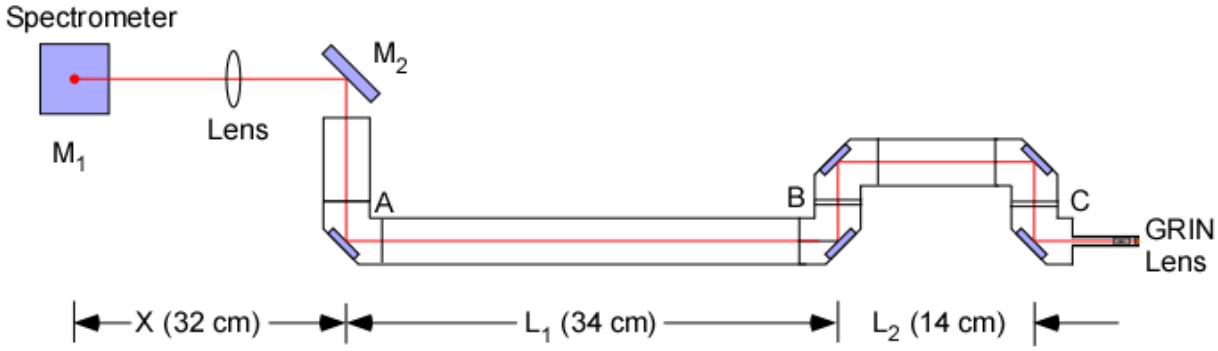

Fig. 3, above. Layout of the optical system, from the spectrometer to the GRIN lens. The arm twists around one axis at point A, and two axes at points B and C, so that the GRIN lens can be pointed in any direction within the working volume. The total path length is 1.1 meters.

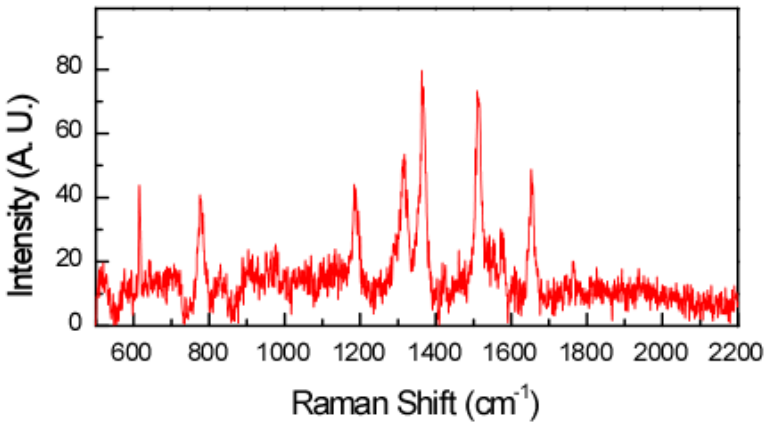

Fig. 4, left. Spectrum obtained of gelatin specimen prepared with 1 mM of R6G and viewed with the system in Figure 3.