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Rugged Fiber Optic Probes and Sampling Systems for Remote Chemical Analysis Via the Raman Technique (U)

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Introduction

IR spectroscopy is the major technique employed by industrial analytical laboratories for process control. However it suffers from several drawbacks that make it difficult to use for remote, real-time, chemical analysis and process control in an industrial environment. Raman spectroscopy overcomes one of the major drawbacks in that it works on solids and slurries as well as clear liquids and gases. Furthermore Raman is well suited for fiber optic implementation since the transmitted and collected light can be in the visible or near-IR wavelength region where the light, unlike IR, can be transmitted great distances through normal glass fibers with little loss. The information obtainable from the optical spectra is of the same quality as that obtained with IR absorption but is complimentary in that some species have strong Raman peaks but not IR peaks and vice versa.[1]

Fiber optics allows the use of Raman spectroscopy in hazardous environments with the placement of a minimal amount of equipment in the hazardous area. Many researchers[2345] have investigated the components of the optimum fiber optic Raman system. These investigations have spurred the development of thermoelectrically-cooled CCD detectors, high power external cavity diode lasers, diode-pumped solid-state lasers, low f-number spectrometers and elegant fiber optic Raman probes. This in turn has lead to the complete commercial systems that are available today. Only the fiber optic probe must interface directly with the process, but to be used in an industrial environment rather than a laboratory setting it should be rugged, easily fabricated and maintained. The design for such a probe will be discussed in the first part of this paper.

Although using the Raman technique for gas analysis is at a disadvantage when compared to mass spectral analysis and gas chromatography due to the low sensitivity of the technique, there are some special cases where it is preferred due to its discriminating power or the fact that it can be done remotely in the case of hazardous or corrosive gases in the process stream. To overcome this low sensitivity a pressurizing sample system may be incorporated into the process interface and the design of such a system will be described in the second part of this paper.

Rugged Raman Probe

Figure 1 illustrates the basic components of a fiber optic Raman system. The laser light is delivered through the central member of the fiber optic probe to the sample where the laser light scatters inelastically off of the sample molecules and the scattered light is collected by the six surrounding fibers in the probe. This light is carried back to the spectrometer where the unshifted laser light, which accounts for most of the light intensity, is removed by a holographic notch filter before it enters the spectrometer. The six fibers are stacked vertically along the spectrometer slit and light entering the spectrometer is dispersed and recorded at all wavelengths of interest simultaneously by the CCD detector.

The optimum geometry of multiple-fiber probes has been investigated previously.[67] SRS has developed a rugged, simply constructed diffuse reflectance probe with a geometry as shown in Figure 2.[8] This design serves as the basis for a Near-IR (NIR) diffuse reflectance probe and the more sophisticated probe for Raman scattering measurements. For Raman measurements, laser light is sent down the central fiber and scattered light is collected by the surrounding six fibers. For diffuse reflection measurements, white light is transmitted through the six outer fibers and scattered light is returned by the central fiber. By angling the faces of the six outer fibers, their light cones are bent inwards due to refraction and therefore cross the light cone of the central fiber at a common point near the tip of the probe. This design concentrates the sample volume near the probe tip and, in an opaque slurry or solid, signals typically are enhanced by factors of five to ten when compared to flat-tip fiber probes.

This design produces a very rugged probe with no optical alignment problems since lenses are not required. Furthermore it is easier to fabricate than the alternative technique of angling the outer fibers so that the acceptance cones cross near the probe tip.[9] When used in liquids, however, a window must be placed over the end of the probe so that the index of refraction of the medium adjacent to the fiber will be constant and smaller than that of the silica. Usually a thin sapphire window is inserted in the dead zone at the probe tip before the source and collection light cones intersect in order to minimize crosstalk between source and pickup fibers. The window is gold-brazed into a metallic or ceramic tube and provides the additional advantage of a hermetically sealed cover to protect the probe tip from the process. Due to the small signals involved when doing Raman measurements via fiber optics, several issues must be addressed beyond those for a diffuse reflectance absorption measurement. These include minimization of the normal sample-induced scattered and reflected light returning to the spectrometer, as well as reduction in the fluorescence and silica Raman scattering generated in the fiber itself. Removal of this noise is accomplished by placing optical filters near the probe tip. Light from the excitation fiber passes through a narrow bandpass filter which transmits the laser frequency but rejects signals arising from the fiber (silica Raman and fluorescence) and extraneous light from the laser source (plasma lines, fluorescence, or superluminance). Light returning through the collection fibers passes through a long pass optical filter which rejects scattered and reflected laser light but transmits Raman and fluorescence signals from the sample.

In order to make a more rugged fiber optic probe for Raman measurements on solids or slurries of the type expected from the chemical processes at Savannah River Site (SRS), we have designed a probe that eliminates as many optical elements and surfaces as possible. This probe is illustrated schematically in Figure 3. The diffuse reflectance probe tip is modified for Raman scattering measurements by installing thin dielectric in-line filters in the last 3-inch sections of the fibers. These filters are sandwiched between fibers held in standard SMA connectors. Probe tips and filters can be easily replaced in case of damage or the need to change laser excitation frequency. The probe is inexpensive ($800/probe) and easily fabricated without precision optical elements or complex alignment procedures. Furthermore, the sample-probe geometry is very reproducible, since the probe window is placed in contact with the sample rather than being held at a fixed standoff distance. The most efficient probe design, however, uses six collection fibers, which can be expensive because of fiber cost ($60/meter) if long fiber runs are required.

Figure 4 shows the effect of each of the optical filters on the Raman spectrum from a powder of $NaNO_3$. The laser source is a 780 nm diode laser, delivering 20 milliwatts to the probe tip. By placing a laser pass filter in the excitation fiber the superradiance and fluorescence background from the laser is removed and the silica Raman is significantly reduced. When the laser rejection filter is put into the collection fibers the remaining silica Raman is reduced to a very low level.

By using a diode laser excitation at 780 nm the fluorescence in the samples is greatly reduced over that obtained with traditional sources such as Argon ion (488 nm , 514.4 nm) or Neodymium-YAG (532 nm). This allows one to obtain excellent spectra from organic solids such as illustrated in Figures 5 and 6, where the Raman spectrum may be obscured by the fluorescence in some cases when using the traditional laser sources. The Raman spectrum of a Tylenol tablet as shown in Figure 5 illustrates the 'fingerprint' region and total spectral coverage of the system. The potential use of the technique for distinguishing between the various types of plastics is illustrated in Figure 6. These results hint at the potential commercial use of this technique for quality control in the pharmaceutical industry in the former case and the plastics recycling industry in the latter.

At SRS, fiber optic Raman probes are being developed for the in situ chemical mapping of radioactive waste storage tanks to answer questions about homogeneity and stratification. Waste tank contents are caustic slurries of metal hydroxides and crystallized nitrate salts at temperatures up to 90 C and radiation fields up to 10,000 RAD/hour. Radiation severely darkens silica fiber optics at ultra-violet and visible wavelengths, but our testing has shown that darkening effects are negligible for wavelengths beyond 700 nm. Probe designs for interfacing to corrosive chemical processes are being evaluated jointly between SRS and commercial chemical manufacturing companies. Other uses of Raman spectroscopy at SRS are identifying organic pollutants in soil by deploying the probe in a cone penitrometer, and measuring hydrogen, nitrogen, and oxygen gas mixtures in the off-gas from certain SRS processes. It is this latter application that is discussed in the next section.

Measuring Process Gases with a Fiber Optic Raman Spectrometer

Hydrogen evolution creates flammability issues for many industrial chemical processes. In many of these cases nitrogen purging of the critical space assures nonflammable conditions (less than 4.0% in air), however, actual measurements are desired to confirm safe hydrogen concentrations during operation. None of the available simple hydrogen or combustible gas sensors on the market were found suitable for operation in the chemical environment at SRS due to unreliability, interferences from other gases in the offgas stream, and/or poisoning of the sensor from corrosive components in the gas stream. Of the currently commercially available techniques a gas chromatograph was determined to be the most suitable instrument for this measurement, but practical problems with installing and maintaining it in a highly contaminated area have lead to development of alternative technologies. Since fiber optic spectroscopy is a powerful remote measurement technique, it is considered the best candidate for an alternate technology.

Overview of System

The components of the fiber optic Raman hydrogen detector were chosen to give a sensitivity to allow the detection of hydrogen concentrations at levels less than 0.1% with a measurement time less than that of a typical GC measurement, which is about 90 seconds. Theoretically it would be possible to achieve these goals by exciting the sample directly with a powerful laser. However to achieve this sensitivity a laser with a power greater than 13 watts would be required and this power level would lead to further complications arising from nonlinear effects generated in the fiber optic cable as well as a high energy density at the probe tip. A laser of this power would also would require cooling water, special power and would have a much shorter lifetime under continuous operation conditions required than the lower power laser used in this system. Since it was desired to minimize the required space for installation and to minimize maintenance requirements, the system described below with a smaller laser and a sample pressurization cell to increase the number of gas molecules in the sample volume was deemed a better solution.

Laser and Spectrometer

The laser chosen was an Adlas model DPY-425II. This is a frequency-doubled NdYAG laser with a maximum power of 420 milliwatts and is pumped by a bank of solid-state diode lasers. The laser emits a 532 nanometer beam and was chosen because it is smaller in size and uses much less energy than any gas laser alternative. As a result it can be powered by 110V instead of 220V and requires no cooling water. In addition, the mean time between failures (mtbf) is estimated to be 10,000 hrs versus 2000 hrs for the gas laser. The spectrometer is a Spex 270M, which is a 0.27 meter, F/4, imaging spectrograph. A grating optimized for 500nm and with a dispersion of 6nm/mm was chosen so that the spectral coverage on the 1 inch detector includes all lines between the laser line at 532nm and the hydrogen vibrational Raman line at 683.0 nm (4160 cm-1 Raman shift). This coverage will allow the simultaneous observation of the nitrogen and oxygen vibrational lines at 607.3 nm (2331 cm-1) and 580.0 nm (1556 cm-1) for real-time verification of operation and calibration. The spectrograph resolution of 0.5nm assures that 10 pixels correspond to the full width at half maximum (FWHM) of an optimized Raman line.

Pressurizing Sample System

In order to achieve the desired sensitivity, a pressurizing sample system was developed to interface to the process gas stream. This system consists of a 1 1/8 inch diameter bore, stainless-steel pressure cylinder with a motorized linear actuator for applying the necessary force to the piston for compressing the gas in the cylinder. The maximum stall force on the motor is 500 lb. and leads to a maximum pressure of approximately 500 psi. This limitation on motor output guarantees safe operation since the cylinder is rated at greater than 500 psi. This cylinder may be disassembled for ease of maintenance and modification. The sample volume illuminated by the laser probe is incorporated into the end of the cylinder in order to reduce the sample volume and thereby reduce the size and complexity of the overall system as well as the cycle time for a measurement.

The sample system is shown schematically in Figure 7. The tip of the fiber optic probe screws into the end plate of the cylinder which has been modified by silver soldering a standard stainless steel SMA fiber optic coupling. The probe has an o-ring over the tip which provides a seal with this coupling. In a second version the cylinder end face has a sapphire window gold-brazed on the inside surface over the hole. This brazed window provides a more secure hermetic seal thus protecting the fiber optic probe from exposure to the process gas and facilitates maintenance on the probe.

A schematic of the sample loop is also given on Figure 7. The process gas sample is injected and pre-pressurized to 30 psi by a small diaphragm pump. The 1.5 psi check valve on the inlet side of the sample cylinder admits gas during suction but provides a seal during the compression stroke. A computer controlled valve on the outlet side is opened to allow flow through the cylinder for exhausting the sample after measurement. The pressure is monitored with an all stainless steel pressure transducer which provides a 0-10V signal that is input into the computer using an Opto22 A/D module (AD6). The motion of the linear actuator and the exhaust valve are controlled via relays which are in turn activated using an Opto 22 digital I/O module(ODC 50). These relays control the direction of motion of the actuator, but the starting and stopping positions are controlled by limit switches.

Sample Probe and Sample Chamber

The standard six-around-one Raman probe is used for this system, however the inline filters are not necessary for this measurement since the vibrational line for hydrogen is far removed from the silica Raman and fiber fluorescence lines that must be removed spectra for other applications. The unshifted laser light scatters off of the walls of the cylinder and the piston and contributes to a large flat background in the spectrum. Any background due to interaction with the walls of the sample chamber or films on them is removed by using a self-referencing technique. A measurement taken before the compression stroke is subtracted from that taken at the end of the compression stroke. Although this removes the background, the statistical noise in the measurement is still increased due to the larger number of counts involved. In order to minimize the background, and thus total counts in the spectrum, a thin light-absorbing disk of carbon is attached to the piston. The six fibers for collecting the scattered light increases the signal by six-fold. However the multiple fibers presented at the slit require a larger number of the vertical pixels for the image on the CCD detector and limits the number of simultaneous sample points that can be observed with a single detector. One might think that using a smaller core fiber would allow one to fit more probes onto the CCD image area; however, fiber with a 200 micron core was tried and the signal was reduced significantly compared to the 400 micron probe. For this reason fiber with a core size of 400 microns is used in the probe construction.

Software

All functions of this prototype are automated and controlled by an IBM PC (486-66mhz). The computer communicates through an RS232 connection with an opto22 brain board controller. This controller provides the digital signals to control relays that in turn control the exhaust valve and linear actuator. It also converts the analogue signal from the pressure transducer into a digital signal to output to the computer. The CCD detector has a bus card for its control and data I/O. The detector control software is written in C-code and is provided by the manufacturer. In addition the spectrometer may be controlled through an RS-232 connection and one can change slit width, chose one of two gratings, and move the grating under computer control. However these items should remain fixed during operation and are only used for diagnostics. The automated control program is written in Visual Basic for Windows with a dynamic link library (DLL) provided that includes the detector control software. This program is designed to provide a very user-friendly interface for the operator. The software is adapted from a software package which has been developed for use on all on-line spectroscopic instruments at SRS. It contains the necessary chemometric routines for robust, on-line analysis of spectroscopic data and, since it is modular in nature, it was straight forward to modify it for use on this instrument.

Operation

A typical measurement cycle takes less than 50 seconds. The exhaust valve is opened while the pressure cylinder is in the extended position and the sample chamber is flushed. The valve is closed and a new sample is injected by the diaphragm pump to a pressure of 30 psi. A 20 second integration on the detector is executed to acquire a background spectrum. The computer then initiates a compression cycle by extending the linear actuator. The computer waits for 5 seconds until the actuator has time to reach its limit switch and the pressure has reached a steady value near 500 psi. The pressure reading is then input via the opto22 to the computer for correcting the data and verifying that the valves are not leaking. A second 20 second integration is then initiated on the detector. The background spectrum is subtracted, the data is smoothed and any residual background is subtracted. The peak height of the hydrogen peak is determined and, after a correcting for any difference between the actual pressure and the calibration pressure of 500 psi, the hydrogen concentration is determined. The linear actuator is retracted until the limit switch is reached and the exhaust valve is opened for 5 seconds of sample flush to complete the cycle.

Verification Testing

In order to verify operation of this prototype calibrated sample gases were obtained from Scott Specialty Gases. This gas consisted of 2% hydrogen and 0.5% nitrogen dioxide with the balance nitrogen. A typical Raman spectrum for a 20 second integration time at a pressure of 465 psi is shown in Figure 8. Both the nitrogen and hydrogen vibrational peaks are visible in this plot. The data displayed is the result of subtracting the spectrum at 30 psi from that at 465 psi followed by a smoothing of the data with a 5 point gaussian fit and subtraction of a small, broad residual background. In order to calibrate the instrument and measure the signal to noise ratio, the pressure of this sample was varied between 0 and 500 psi. As the pressure varied the number of molecules of hydrogen in the sample cell varied and this could be related to a concentration at 500 psi that would give this same number of molecules according to the formula,

(1) $$c = 2\% * P/500$$

where c is the concentration at 500 psi and P is the measured pressure. Since the Raman signal is proportional to the number of molecules and neither the signal nor the noise is dependent on the pressure if the number of molecules is kept fixed, it is possible to infer the variation of the Raman signal for hydrogen as a function of concentration using this calculated concentration. A least squares linear fit to the peak height of the hydrogen Raman signal versus this calculated concentration gives a goodness of fit as illustrated in Figure 9. Here the concentration predicted from this fit is plotted versus the actual concentration given by equation 1. The slope or correlation constant is 0.9986, and the statistical error in a concentration is 0.022% over this range.

This performance verifies the stated specification of 0.1% detectability limit for hydrogen in nitrogen in the presence of NO2 as an interferent. The effects of moisture on the measurement have been investigated by bubbling the calibration gas through water, and no interference or increase in background signal was observed. It would be worthwhile to more closely look at this and other effects such as film growth on the interior surface of the sample chamber as might be expected after prolonged operation in the corrosive atmosphere of some potential offgas streams.

One obvious application of this instrument would be determining gas concentrations in gas mixing operations as might be encountered in filling or certifying already filled compressed gas cylinders for industrial or research use. The system's remote capability using fiber optics would be especially useful for dealing with hazardous gases. The technique also has an advantage over GC or MS analysis since the sample does not have to be transported to the measuring instrument either by manual sampling or side stream piping. If the gases are already being compressed for storage, the pressurizing sample system can be eliminated and only the Raman probe need be interfaced to the cylinder or gas line. The real-time feedback capabilities of this system would also be useful for controlling gases in a chemical process. An example of the Raman spectrum obtainable from a complex mixture of gases used for GC calibration is shown in Figure 10 and Table 1 gives Raman shifts and cross sections relative to that of nitrogen for some gases of potential interest.

For decades Raman spectroscopy has been confined to research laboratories because instruments were large, complex and expensive, and because results required expert interpretation. Recent technological advances in fiber optics, diode lasers, CCD detectors, dielectric and holographic optical filters, grating spectrometers, and chemometric data analysis have greatly simplified the practice of Raman spectroscopy. Raman spectroscopy via fiber optics is ready to move out from the research laboratory and into the real world and provides a powerful tool for process analytical chemistry.

Table 1: Raman Shifts and Cross Sections for Gases

Molecule	Raman Shift(cm-1)	Cross section relative to Q-branch of N2
CCl_4	459	9.3
$NO_2(v_2)$	754	8.6
SF_6	775	4.3
O_3	110.3	2.3
SO_2	1151.5	6.1
$CO_2(2v_2)$	1285	1.1
NO_2	1320	18.2
$CO_2(v_1)$	1388	1.5
O_2	1556	1.6
C_2H_4	1623	1.9
NO	1877	.54
CO	2145	1.3
N_2	2330.7	1.3
H_2S	2611	6.8
CH_4	2914	11.5
NH_3	3334	3.9
C_2H_2	3372	1.2
H_2O	3651.7	2.8
H_2	4160.2	3.1

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[9] R. D. McLachlan, G. L. Jewett and J. C. Evans, U.S. Patent No. 4,573,761

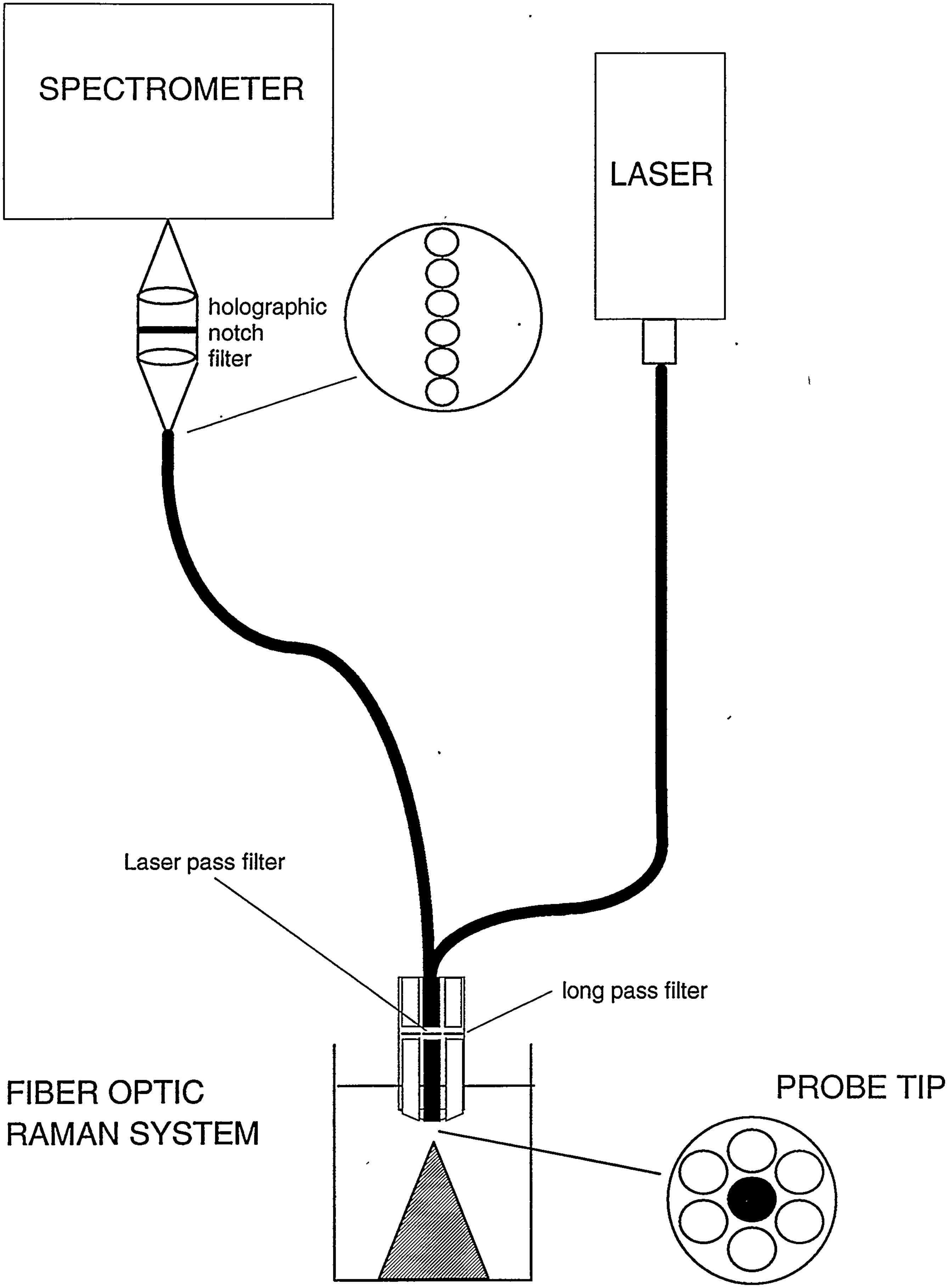
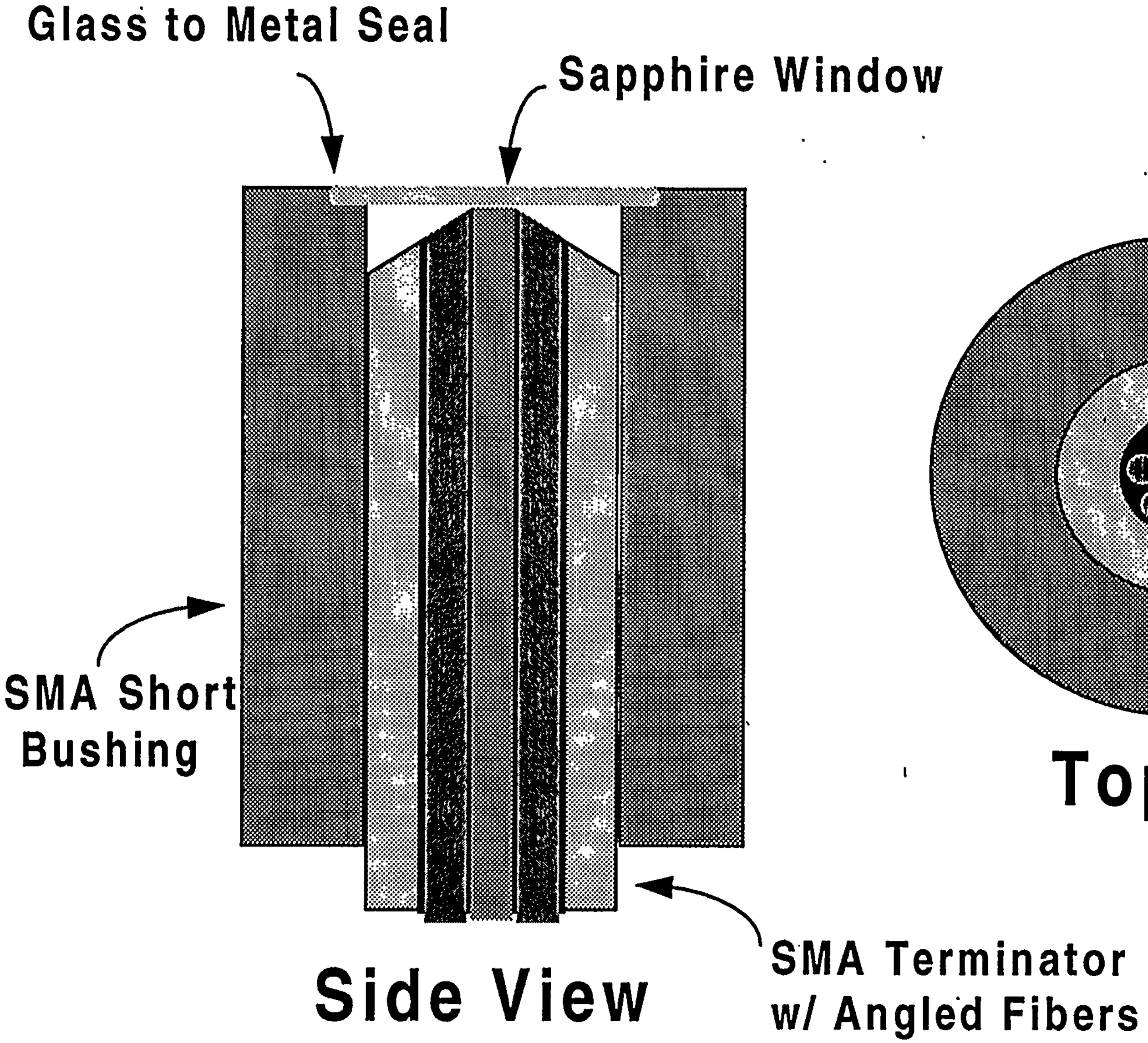

SPECTROMETER
LASER
holographic notch filter
Laser pass filter
long pass filter
FIBER OPTIC RAMAN SYSTEM
PROBE TIP

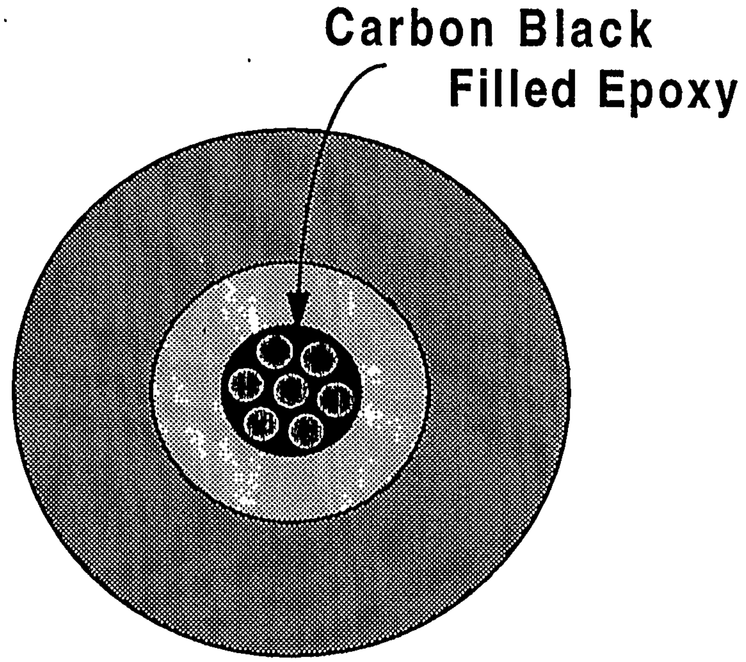
Figure 1

Figure ~~5~~ 2

Seven Fiber Scattered Light Probe



Side View



Top View

Raman Probe

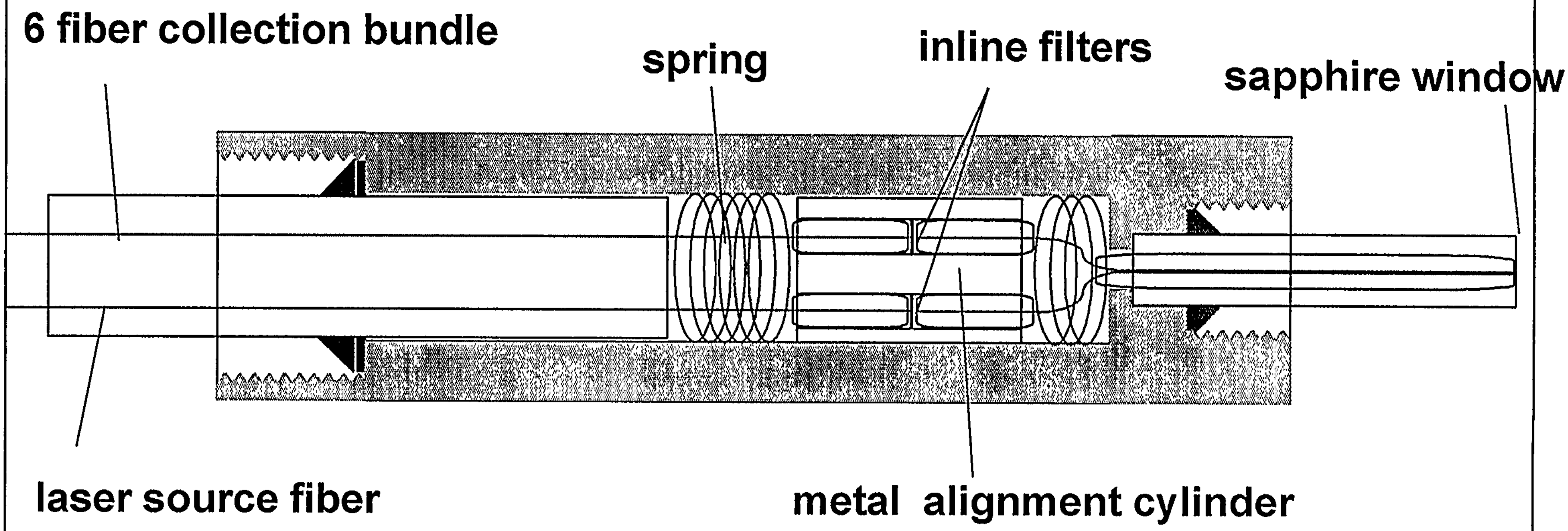


Fig 3

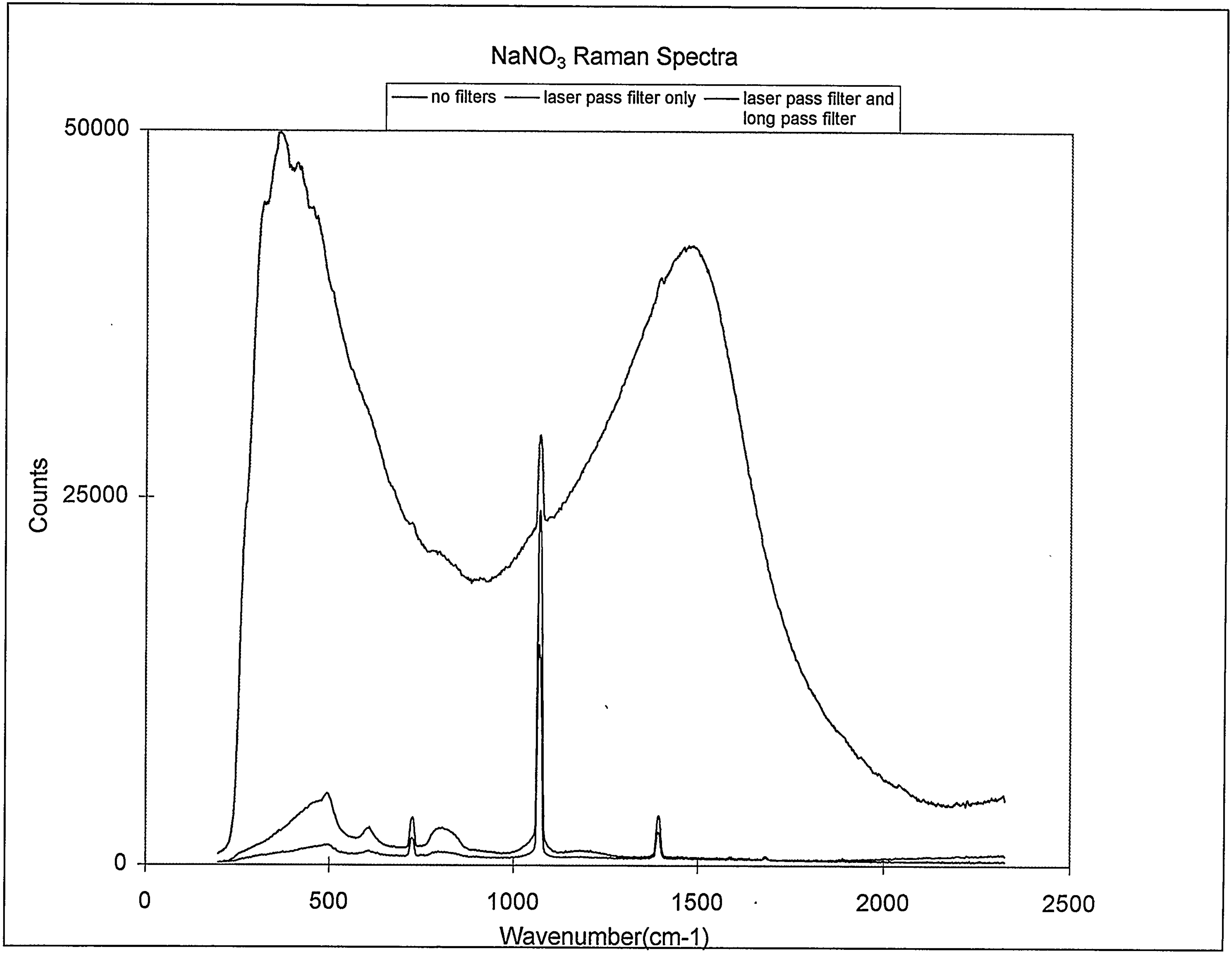

NaNO3 Raman Spectra
no filters
laser pass filter only
laser pass filter and long pass filter
50000
25000
0
Counts
0
500
1000
1500
2000
2500
Wavenumber(cm-1)

Fig 4

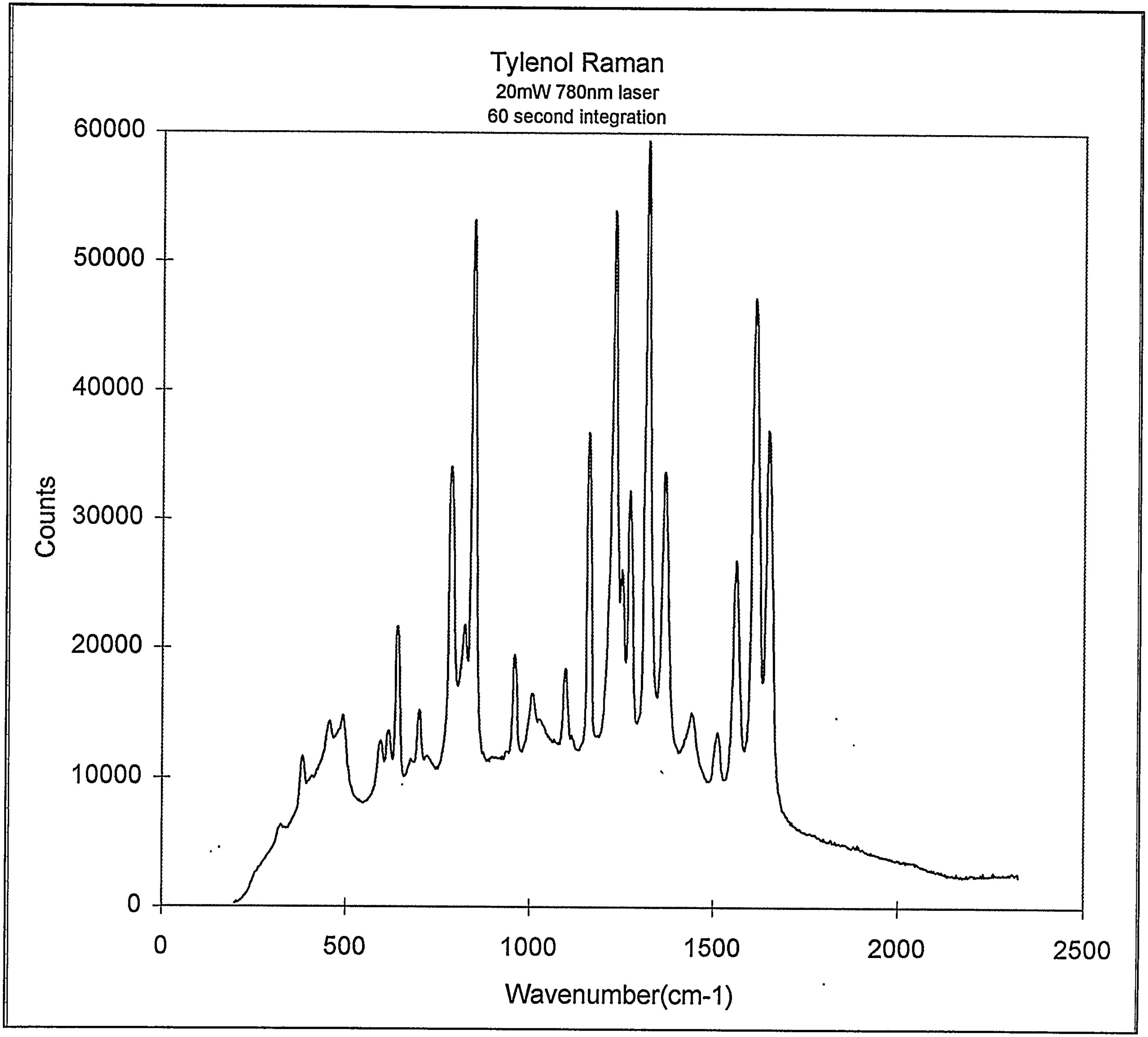
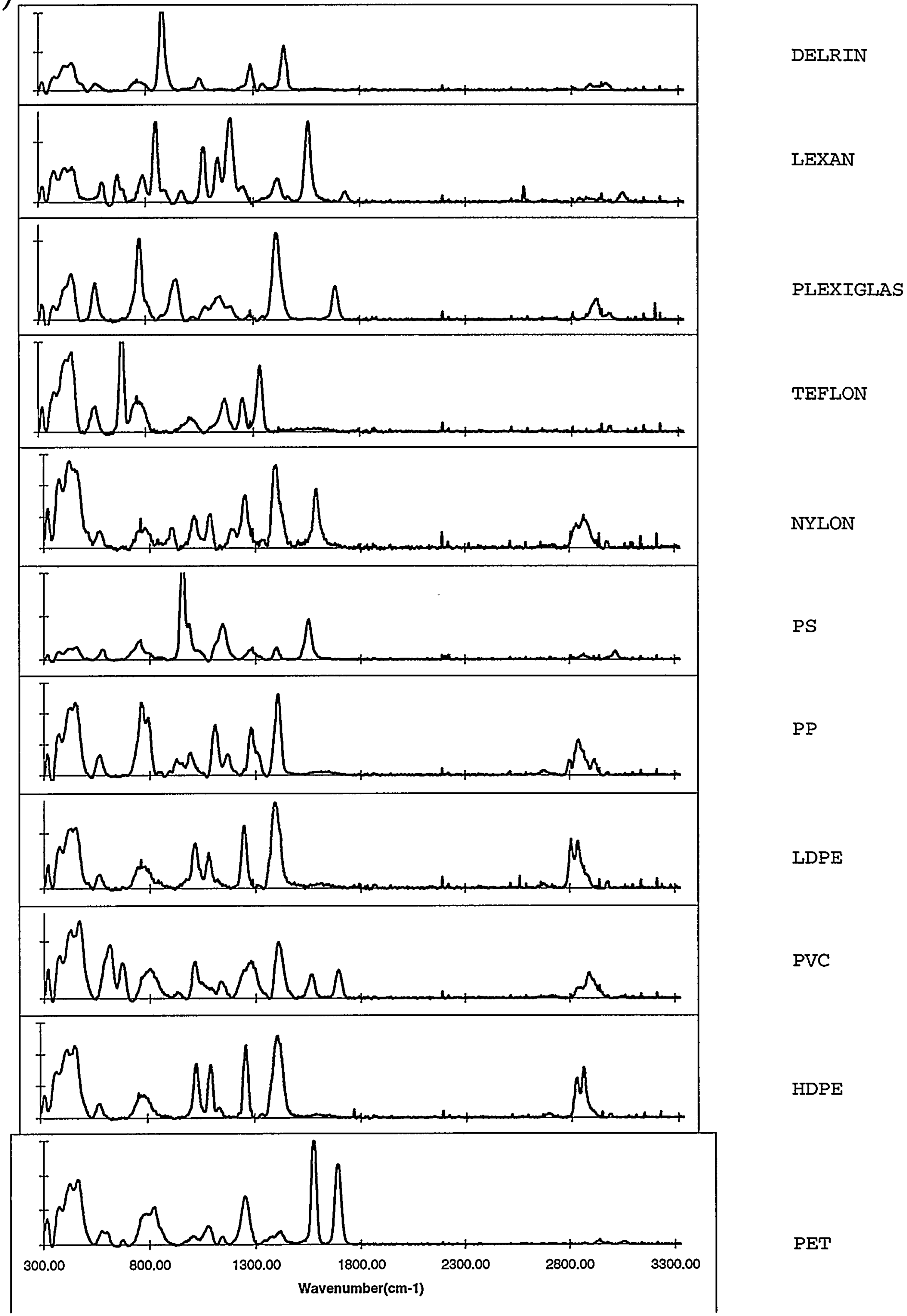

Tylenol Raman
20mW 780nm laser
60 second integration
Counts
60000
50000
40000
30000
20000
10000
0
0
500
1000
1500
2000
2500
Wavenumber(cm-1)

Fig 5

Figure 6 – RAMAN of PLASTICS USING a 780nm LASER



Pressurizing Sample System

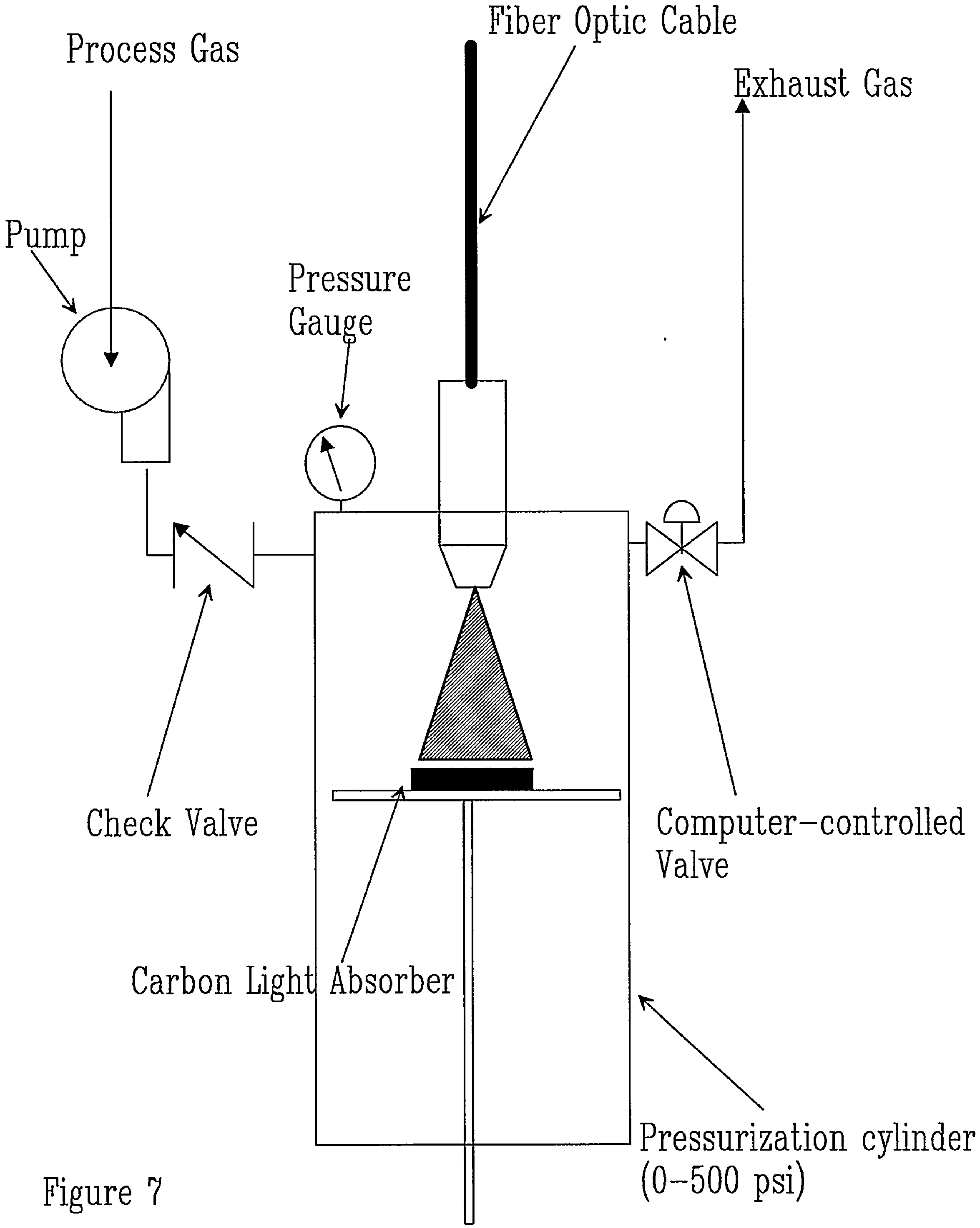


Figure 7

Figure ~~6~~ 8

Raman of 2% H_2 in 0.5% NO_2 balance N_2 at 465 psi

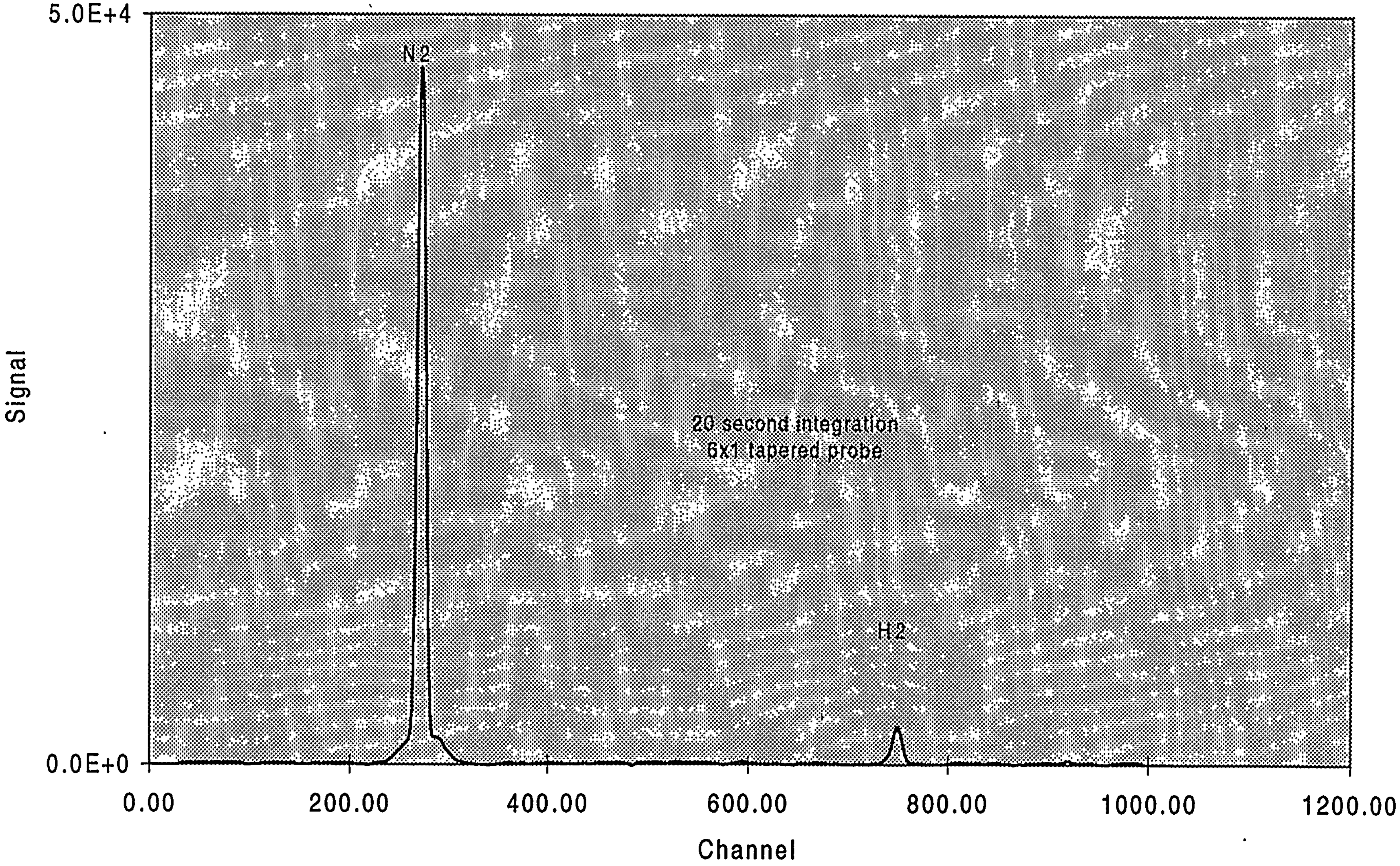
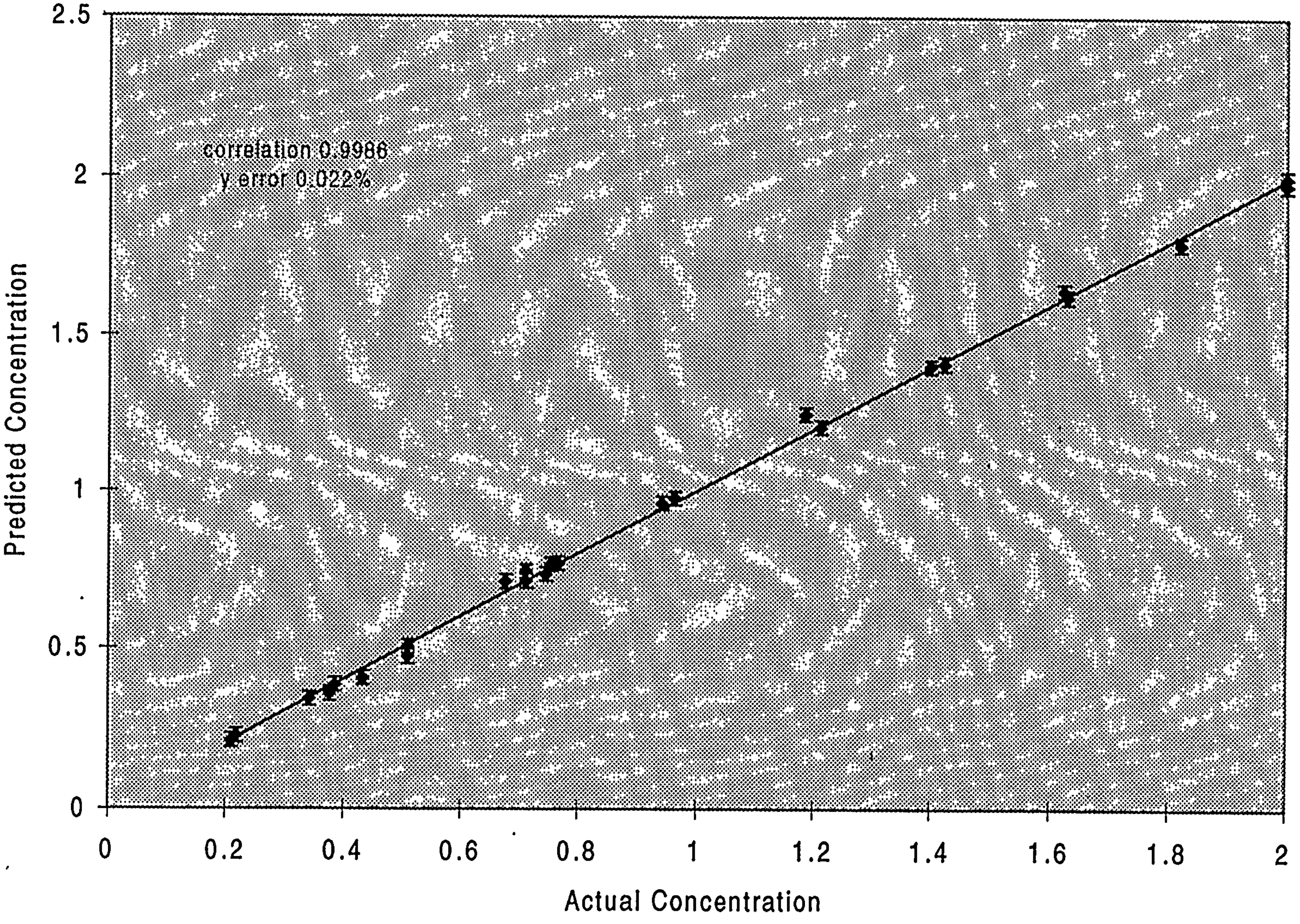


Figure 19

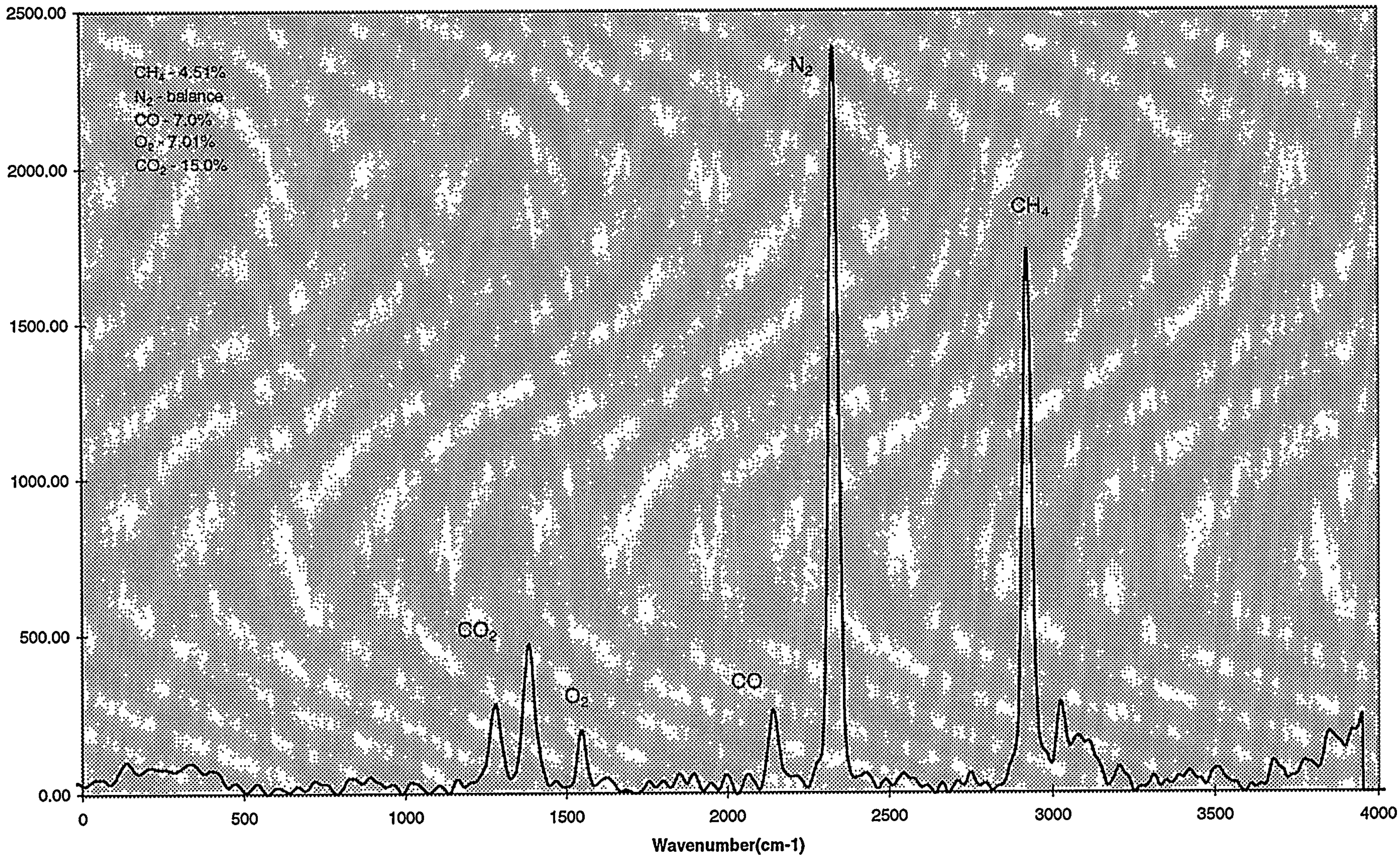
Calibration Data for Fiber Optic Hydrogen Raman
0.5% NO2 - balance nitrogen



MMGAS Chart 1

Raman of Gas Mixture :

200mW 532nm 240PSI



~~Page 1~~

Figure 10