

the sample, a choice of the tolerable error level, and a choice of the tolerable probability of obtaining a "good" result by random chance. From these chosen numbers one can determine the required number of samples from the presented figures. This objective procedure should decrease the workload of near-infrared correlation spectroscopy methods development and increase their reliability.

#### ACKNOWLEDGMENT

Supported in part by the Office of Naval Research, by the U.S. Department of Energy under contract W-7405-ENG-48 and by a grant from the Technicon Instrument Corporation.

1. W. H. Hunt, D. W. Funk, B. Elder, and K. H. Norris, *Cereal Foods World* **22**, 534 (1977).
2. P. C. Williams, K. H. Norris, R. L. Johnsen, K. Standing, R. Friconi, D. MacAffrey, and R. Mercier, *Cereal Foods World* **23**, 544 (1978).
3. G. S. Birth, *J. Food Sci.* **44**, 949 (1979).
4. W. R. Hruschka and K. H. Norris, *Appl. Spectrosc.* **36**, 261 (1982).
5. J. B. Kennedy and A. M. Neville, *Basic Statistical Methods for Engineers and Scientists* (Harper & Row, New York, 1976), 2nd ed., p. 449.
6. T. W. Anderson, *An Introduction to Multivariate Statistical Analysis*. (John Wiley and Sons, Inc., New York, 1958), p. 89.
7. *Handbook of Mathematical Functions*, M. Abramowitz and I. Stegun, Eds. (U.S. Government Printing Office, 1964).
8. J. B. Kennedy and A. M. Neville, *Basic Statistical Methods for Engineers and Scientists* (Harper & Row, New York, 1967), p. 460.

## Development of a New Optical Wavelength Rejection Filter: Demonstration of Its Utility in Raman Spectroscopy

PERRY L. FLAUGH, STEPHEN E. O'DONNELL, and SANFORD A. ASHER

*Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*

A new tunable optical filter has been developed which rejects a narrow wavelength interval ( $<7.5$  nm) in the near-UV, visible, or near-IR spectral region and allows adjacent wavelengths to pass ( $T > 90\%$ ). This filter will be useful in optics, in spectroscopy, and for laser applications. The active element of the filter is a crystalline colloidal array of polystyrene spheres. The rejected wavelengths are Bragg diffracted from this ordered array. For a particular sphere concentration and scattering from a particular set of lattice planes, tunability can be achieved by the altering of the angle between the filter and incident light beam. Bragg diffraction and light rejection of these filters are monitored by transmission measurements. The utility of this filter for spectroscopic measurements is demonstrated for Raman spectroscopy. Raman measurements are shown for polypropylene, a highly scattering material with numerous low-frequency modes. The filter selectively attenuates the elastically scattered light and allows the low frequency peaks to be observed. Use of this wavelength rejection filter to reject the Rayleigh scattered light simplifies the instrumentation, decreases the cost, and increases the sensitivity of Raman spectral measurements. This filter also has the potential to replace dispersive elements such as gratings and prisms in a variety of spectroscopic and optical applications.

Index Headings: Instrumentation, emission spectroscopy; Filters; Ar<sup>+</sup> lasers; Light scattering; Optics; Reflectance; Raman spectroscopy; Techniques, spectroscopic; Visible UV spectroscopy; X-ray diffraction.

#### INTRODUCTION

Numerous optical techniques require wavelength-selective optical elements to pass or reject particular regions of the electromagnetic spectrum. For example, the common color filter is used to isolate a particular wavelength interval by absorbing light at wavelengths outside the region of interest. In general, these filters do not have sharp band edges and thus are not useful for efficiently separating wavelengths within 20–30 nm of each other. Multilayer dielectric filters can be obtained with narrow bandpasses of less than 7.5 nm and with

maximum throughputs at the center wavelength of greater than 30%. Thus, these filters can be used to select a small wavelength interval. These filters also exhibit tunability, since changing the angle of the filter to the incident light beam results in a change in the band-pass center wavelength.

In many applications, it is necessary to reject one particular wavelength while passing all adjacent wavelengths. Typical examples include fluorescence measurements, Raman spectroscopy, and the many pump-probe techniques. These pump-probe techniques include photochemical transient absorption studies in which a pump beam at a particular wavelength excites the sample, and a polychromatic, or monochromatic, probe beam at another wavelength is used to monitor absorption changes. Another example occurs in the thermal grating experiment,<sup>1</sup> where a pump beam generates a thermal grating in a sample and a probe beam at a second wavelength is diffracted from the grating. The magnitude and temporal behavior of the diffracted intensity monitors the sample absorption and thermal diffusion, respectively. Monochromators are used in all of these applications to select the spectral region to be passed and to reject the pump wavelength.

The use of monochromators offers tunability and wavelength selectivity. The selectivity depends on the bandpass of the monochromator. However, for very high rejection efficiencies ( $>10^4$ ) multiple gratings must be used in order to reduce the "scattered light" from the gratings and other optical elements in the monochromator. For those optical experiments where the probe beam intensity is weak compared to the intensity of the light scattered from the pump beam, or where the signal intensity is weak compared to the intensity of the exciting beam, high wavelength selectivity is required to reject the pump wavelength, and double or triple monochromators are required. This is especially true for

Received 10 February 1984.

techniques such as Raman spectroscopy and fluorescence measurements of weakly fluorescing samples. Unfortunately, these multiple dispersing monochromators are expensive and result in a loss of signal throughput. Typically the throughput is less than 10% for a double monochromator, even close to the grating blaze, and the throughput decreases to less than 3% for a triple monochromator.

In this report, we demonstrate the existence of a new tunable optical filter which is highly efficient and which can replace monochromators for many applications.\* This novel filter rejects a narrow wavelength interval with a rejection ratio greater than  $10^4$  and with a rejection bandwidth of less than 7.5 nm. The active element of the filter is a crystalline colloidal suspension of monodisperse polystyrene spheres.

The formation of crystalline order in colloids has been previously documented in systems as diverse as dispersions of polystyrene latex spheres in various solvents such as water, methanol and benzene,<sup>2-18</sup> proteins,<sup>19</sup> virus particles,<sup>20</sup> bacteria,<sup>21</sup> cell suspensions,<sup>21</sup> and AgI particles.<sup>21</sup> Crystalline ordering for monodisperse polystyrene sphere colloids has been observed for sphere diameters between 0.02–1.0  $\mu\text{m}$ . These monodisperse polystyrene spheres are prepared by emulsion polymerization<sup>7,15,16</sup> followed by size exclusion chromatography. This procedure yields a very narrow size distribution with a relative standard deviation of less than 1%.

A persulfate initiating catalyst is used in the polymerization process and approximately 2000 sulfate groups are bound per sphere.<sup>15,16</sup> Because the sulfate groups ionize in solution, a large negative charge resides on each sphere and the major intersphere interactions are screened coulombic repulsive interactions. This repulsive interaction occurs over distances many times larger than the sphere diameter. Since the spheres cannot leave the solution, they crystallize into an ordered array to minimize the system's net energy. The lattice spacings in the crystal can be made comparable to the wavelength of visible light (*vide infra*), and thus, Bragg diffraction of light will occur.

The crystal structure and lattice parameters of the polystyrene sphere dispersions depend on sphere number density.<sup>2,5-7</sup> Previous studies of polystyrene sphere dispersions indicate a face-centered cubic structure at high sphere concentrations and a body-centered cubic structure at low concentrations.<sup>2,6,9</sup> The presence of electrolytes which screen the repulsive interactions between the spheres also effects the crystal structure,<sup>10</sup> as does the colloid temperature.

In this report, we demonstrate the use of this colloidal system for making narrow band rejection filters and illustrate the use of these filters in Raman spectroscopy.

## EXPERIMENTAL

The polystyrene spheres were obtained from Dow Diagnostics as a 10% aqueous suspension. For the studies reported here, the sphere diameter was 0.091  $\mu\text{m}$  with a

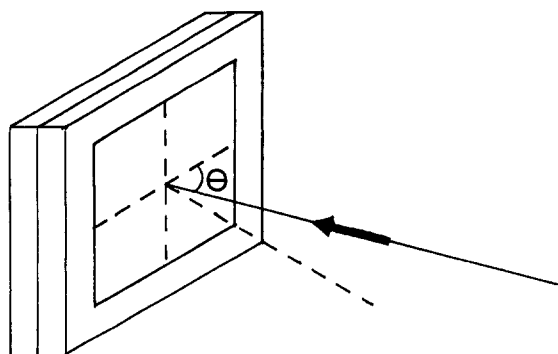


FIG. 1. Wavelength rejection filter showing the angle  $\theta$  between the incident light beam and the plane of the filter.

standard deviation of 0.0058  $\mu\text{m}$ . The filters were made from an aqueous dispersion of these polystyrene spheres. The suspension was freed of electrolyte with a mixed-bed ion exchange resin (Bio-Rad analytical grade AG501-X8), and the suspension was injected into a cell constructed from two pieces of 2"  $\times$  2"  $\times$  1/8" plexiglass separated by a 1/64" Teflon® spacer and sealed with epoxy, except for a small filling hole. With the use of techniques which are described in a recent patent application, crystallization of the colloid was established between the plexiglass plates such that the (111) plane of the face-centered cubic crystal was oriented parallel to the plexiglass surface. The wavelength of maximum rejection and the bandpass of the filters were measured by the use of a Cary 14 or IBM 9420 absorption spectrometer.

Polypropylene microcentrifuge tubes were used as samples for the Raman measurements. The Raman spectra were measured by the use of a Spectra-Physics model 164 Ar<sup>+</sup> laser as the excitation source and a Spex 1401 double monochromator with 5000 Å blazed ruled gratings for wavelength dispersion. The 90° scattered light was collected and measured by the use of photon counting accumulation and detected by the use of an RCA C31034A-02 cooled photomultiplier. A DEC MINC 11 microcomputer interfaced to a stepping motor scanned the monochromator and stored the data.

## RESULTS AND DISCUSSION

Figure 1 shows a perspective drawing of the 2"  $\times$  2"  $\times$  0.265" filter, which contains the crystalline polystyrene colloid. The thickness of the colloid layer is  $\sim$ 0.015". An angle  $\theta$  measures the angle between the incident light beam and the plane of the filter. The apparent absorption spectrum of this filter for ( $\theta = 90^\circ$ ) is shown in Fig. 2. The spectrum indicates that the transmission is less than 1% at the rejection band maximum (limited by the stray light and dynamic range of the absorption spectrometer), and the transmission is greater than 10% and 50% at wavelengths  $\pm 3.0$  nm, and  $\pm 7.5$  nm from the rejection wavelength maximum. We used an incandescent source, the Spex double monochromator, and the photon counting system to measure the transmission at the rejection band maximum and found it to be less than 0.01%. Filters with rejection bandwidths narrower than

\* A patent application was filed December 8, 1983, for this filter in the name of S.A.A.

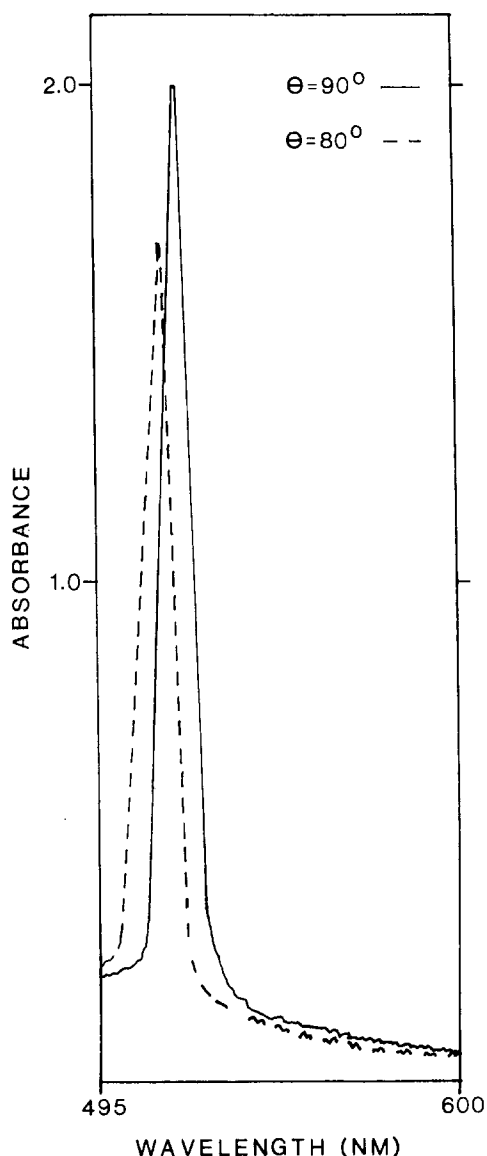


FIG. 2. Absorption spectrum of the colloid filter at  $\Theta = 90^\circ$  and  $\Theta = 80^\circ$ .

6.0 nm can also be prepared by the use of somewhat different conditions. The rejection wavelength maximum for this filter is  $\sim 514.5$  nm for  $\Theta = 90^\circ$ , and thus this filter is ideal for rejecting the green 514.5 nm line of the  $\text{Ar}^+$  laser.

For a particular sphere concentration altering the angle  $\Theta$  between the plane of the filter and the incident light beam changes the rejection wavelength. The diffracted, and, thus, rejected wavelength band fulfills the Bragg condition,  $n\lambda = 2d \sin \Theta$  where  $d$  is an interplanar spacing in the colloid lattice. Thus, as the filter is rotated the diffracted wavelength decreases. For this filter, the longest wavelength diffracted (514.5 nm) occurs for  $\Theta = 90^\circ$  from the set of planes whose normal is along the filter normal. The crystal structure in this filter is face-centered cubic with the (111) plane parallel to the filter plane. Thus, the (111) plane spacing in this filter is 257.2 nm and the lattice parameter is 456.0 nm. By changing the angle  $\Theta$ , the wavelength rejected can be varied. Fig-

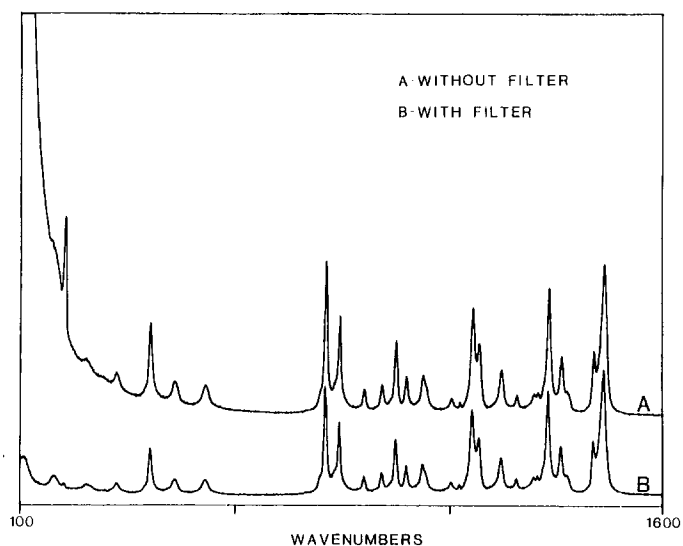


FIG. 3. Raman spectra of polypropylene excited at 514.5 nm: A, without filter, laser power = 0.53 W; B, with filter, laser power = 0.62 W. Both spectra are plotted on the same scale but are offset to make viewing clearer. Integration time = 1.0 s; bandpass  $\approx 3.8$   $\text{cm}^{-1}$ .

ure 2 also shows the observed absorption spectrum for  $\Theta = 80^\circ$  where the rejection band wavelength maximum is 506.7 nm.

As can be seen from the absorption spectrum, this particular filter shows some broadening of the rejection bandwidth as the filter is angle-tuned. This presumably occurs because this filter shows mosaicity with incomplete orientation of the (111) plane parallel to the surfaces of the filter. Better colloid orientation in the filters results in a significantly decreased broadening as the filter is rotated away from  $\Theta = 90^\circ$ .

By the placement of the filter into a collimated beam, a narrow wavelength band is Bragg diffracted out, while adjacent wavelengths which do not meet the Bragg condition are transmitted. Figure 3 shows the Raman spectrum of polypropylene, a highly scattering material with numerous low-frequency modes, excited at 514.5 nm. A high "Rayleigh wing" tail in the low frequency region of this spectrum obscures a low-frequency peak<sup>22</sup> at 171  $\text{cm}^{-1}$  and interferes with the measurement of a low-frequency peak at 254  $\text{cm}^{-1}$ . The rejection efficiency of the double monochromator is insufficient to totally reject the elastically scattered laser light. Normally, a triple monochromator or holographic gratings would be required to efficiently reject the laser light and avoid interference in the low-frequency Raman region. The strong sharp peak at 200  $\text{cm}^{-1}$  appears to be due to a grating ghost (*vide infra*) and not a laser plasma line, since the introduction of a spike interference filter (514.5 nm) in the laser beam did not result in significant attenuation of this peak.

A Raman spectrum of polypropylene utilizing the rejection filter is also shown in Fig. 3. The filter was placed between the collection and imaging lens at the proper angle to reject the laser wavelength. No repositioning of the collection and imaging optics occurred after introduction of the filter. Because the filter selectively attenuates the "Rayleigh scattered light," the low-frequency

Raman peaks become clearly visible in the spectra. The grating ghost observed at  $200\text{ cm}^{-1}$  is also attenuated. Attenuation of the high-frequency modes ( $<600\text{ cm}^{-1}$ ) due to reflection at the filter air-plexiglass interface should be less than 10%. However, the spectrum shown in Fig. 3B indicates that the high-frequency peaks are attenuated by  $\sim 20\%$ , presumably due to a displacement of the image of the collected scattered light off of the entrance slit to the monochromator due to refraction in the filter. The intensity of the high-frequency Raman peaks can be increased by a slight repositioning of the collection optics to properly image the scattered light through the entrance slit of the monochromator. Attenuation of the low-frequency peaks for this filter as calculated from the transmission spectra should be  $\sim 95\%$  at  $100\text{ cm}^{-1}$  and  $\sim 74\%$  at  $200\text{ cm}^{-1}$ .

In the example above, the filter was used to reject a particular wavelength while passing adjacent wavelengths. The Bragg diffracted wavelength is "reflected" from the filter. Thus, used in the reflection mode, the filter can be used as a dispersive element and can be used to replace gratings as wavelength-selective elements.

These filters appear to have significant advantages over the typical dielectric interference filter. For example, greater than 95% of the light is Bragg diffracted, in contrast to the typical narrow-band interference filter, which typically attenuates greater than 50% of the light at the bandpass maximum. In addition, this filter could be used as a dispersive element in a slitless monochromator by scanning techniques similar to that used in  $\Theta$ - $2\Theta$  x-ray diffractometer measurements. A particular wavelength of light would be diffracted onto a PMT from a collimated beam hitting the filter at an angle  $\Theta$ . To change wavelengths, the filter would be rotated about an angle  $\Delta\Theta$  while the detector would rotate by an angle  $2\Delta\Theta$ . In this way, the filter could be used as a slitless monochromator. No additional optical elements are required except for the optics used to collimate the light from the source. The throughput of this monochromator could be greater than 95%.

## CONCLUSION

A novel narrow-band rejection filter is demonstrated which can be used from the near UV ( $\sim 400.0\text{ nm}$ ) into the near IR spectral region ( $1000.0\text{ nm}$ ). The utility of this filter for Raman spectral studies is demonstrated for a highly scattering sample. Only a simple high-dispersion single monochromator or spectrograph would be

required for Raman measurements if this filter were used as a Rayleigh rejection prefilter. This represents a significant savings both financially and in the time required to measure Raman spectra, because of the decrease in the complexity of the monochromator required, and because of the increase in the throughput efficiency of the filter/single monochromator combination. For example, the throughput for the filter and a single monochromator will be  $\sim 30\%$ , in contrast to the characteristic 10% efficiency of a double monochromator and the  $\sim 3\%$  efficiency of a triple monochromator. We predict that this application in Raman spectroscopy represents only the first of numerous applications for this new optical device; additional applications in spectroscopy and optical measurements are obvious.

## ACKNOWLEDGMENTS

We gratefully acknowledge partial support for this work with funds from the University of Pittsburgh and sponsorship by the Commonwealth of Pennsylvania acting through the Board of the Ben Franklin Partnership Fund, the MPC Corporation, and the Western Pennsylvania Advanced Technology Center. We also gratefully acknowledge partial support of this work from NIH grant 1 RO1GM 30741-01.

1. M. J. Pelletier, H. R. Thorsheim, and J. M. Harris, *Anal. Chem.* **54**, 239 (1982).
2. R. J. Carlson and S. A. Asher, *Appl. Spectrosc.* **38**, 297 (1984).
3. I. M. Krieger and F. M. O'Neill, *J. Am. Chem. Soc.* **90**, 3114 (1969).
4. P. A. Hiltner and I. M. Krieger, *J. Phys. Chem.* **73**, 2386 (1969).
5. P. A. Hiltner, Y. S. Papir, and I. M. Krieger, *J. Phys. Chem.* **75**, 1881 (1971).
6. R. Williams and R. S. Crandall, *Phys. Lett.* **48A**, 225 (1974).
7. J. W. Goodwin, R. H. Ottewill, and A. Parentich, *J. Phys. Chem.* **84**, 1580 (1980).
8. N. A. Clark, A. J. Hurd, and B. J. Ackerson, *Nature* **281**, 57 (1979).
9. J. M. Silva and B. J. Mokross, *Solid State Comm.* **33**, 493 (1980).
10. K. Takano and S. Hachisu, *J. Chem. Phys.* **67**, 2604 (1977).
11. S. Hachisu and Y. Kobayashi, *J. Colloid Int. Sci.* **46**, 470 (1974).
12. A. Kose and S. Hachisu, *J. Colloid Int. Sci.* **46**, 460 (1974).
13. C. J. Barnes, D. Y. C. Chan, D. H. Everett, and D. E. Yates, *Chem. Soc. Faraday Trans. II* **74**, 136 (1978).
14. S. Hachisu, Y. Kobayashi, and A. Kose, *J. Colloid Int. Sci.* **42**, 342 (1973).
15. J. W. Vanderhoff, *Pure. Appl. Chem.* **52**, 1263 (1980).
16. J. W. Vanderhoff and H. J. Van Den Hul, *J. Macromol. Sci.-Chem.* **A7**, 677 (1973); *J. Colloid Int. Sci.* **28**, 336 (1968).
17. K. Takano and S. Hachisu, *J. Colloid Int. Sci.* **66**, 124, 130 (1978).
18. M. K. Udo and M. F. deSouza, *Solid State Comm.* **35**, 907 (1980).
19. D. P. Riley and G. Oster, *Discuss., Faraday Soc.* **11**, 107 (1951).
20. K. M. Smith and R. Williams, *Endeavor* **17**, 12 (1958).
21. V. W. Luck, M. Klier, and H. Wesslau, *Naturwissenschaften* **50**, 485 (1963).
22. H. N. Siesler and K. Holland-Mortiz, *Infrared and Raman Spectroscopy of Polymers* (Marcel Dekker, Inc., New York, 1980), p. 66.