Use of Filters for Suppressing Scattered Light in Spectrometers Used in the Ultraviolet

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The range of spectrometers can be extended to wavelengths shorter than 3000 Å in the ultraviolet without modifications which would impair their versatility at longer wavelengths by using an intense source and filtering out the scattered light in the visible and near ultraviolet. An absorption filter composed of nickel sulfate hexahydrate and Corning 9863 glass is described which extends the range of an absolute reflectometer having over thirty reflections and employing a single-beam, double-pass monochromator to about 2400 Å.

Introduction

The need to reduce scattered light when working in the ultraviolet region of the spectrum frequently is not as widely appreciated as it is for infrared measurements. Since multiplier phototubes, the principal detectors used in the ultraviolet, are saturable, it is necessary not only to eliminate chopped, scattered light, which will be erroneously recorded as a signal, but also unchopped light. If excessive unchopped light is allowed to fall on the tube, the response of the tube becomes nonlinear and, in addition, the tube becomes extremely noisy.[1,2] The appearance of additional noise in the signal as the wavelength is decreased thus often indicates that excessive scattered light is present in the spectrometer.

Most of the scattered light present when making ultraviolet measurements is concentrated in the visible and near-ultraviolet regions of the spectrum. It arises from three principal causes. The ultraviolet radiant intensity of most sources decreases rapidly with decreasing wavelength, so that more energy is present in the spectrometer in the visible and near ultraviolet than at shorter wavelengths. The specular reflectance of the mirrors in the spectrometer is larger at the longer wavelengths, making the luminosity of the instrument higher in the visible than in the ultraviolet. Finally, the maximum sensitivity of most commonly used multiplier phototubes occurs in the visible and near ultraviolet. Hence the problem of reducing scattered light present for ultraviolet measurements becomes one of suppressing the longer-wavelength, visible, and near-ultraviolet radiation falling on the detector. Various techniques[3] can be employed, such as the use of double monochromators, hydrogen discharge lamps, and other sources which have a relatively low intensity in the visible, or "solar blind" multiplier phototubes which have a lowered response in the visible and near ultraviolet. However, a simple solution is to block out the unwanted radiation with a filter which absorbs strongly in the visible and near ultraviolet and transmits at shorter wavelengths.

The use of filters for reducing longer-wavelength scattered light when making ultraviolet measurements has been restricted because of the lack of materials which absorb strongly in the visible and near ultraviolet and transmit at shorter wavelengths. Corning 9863 glass* has been used in some instruments,[4] but since it transmits in the near ultraviolet, when the wavelength of interest becomes short enough that scattered light in this region becomes important, some other solution must be found. One of us[5] has developed as a filter material single crystal nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), which, when used with Corning 9863 glass and fused silica, has good transmission in the far ultraviolet and is opaque at longer-ultraviolet and visible wavelengths. This material has been used in both the interference[6] and absorption types[7] of filters for the wavelength region 2000–3500 Å. To date such filters have been used primarily for obtaining a long-wavelength cutoff near 3000 Å in an ultraviolet photometer[8] and as broad-band absorption filters in rocketborne photometric instruments.[6,7] By incorporating the filters in monochromators used in the ultraviolet as well as at longer wavelengths, the range of these instruments can with little difficulty be extended to wavelengths shorter than 3000 Å.

Experimental

The filters used in this experiment were composed of various thicknesses of $NiSO_4 \cdot 6H_2O$ single crystals,† Corning 9863 filter glass,* and Ultrasil fused silica.‡

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* Obtained from Corning Glass Works, Corning, New York.

† Obtained from Semi-Elements, Inc., Saxonburg, Pennsylvania.

‡ Obtained from Engelhard Industries, Inc., Hillside, New Jersey.

Since the $NiSO_4 \cdot 6H_2O$ is hygroscopic, it was protected from the atmosphere by sandwiching it between the 9863 and Ultrasil glasses using appropriate spacers, and edge-sealing the combination filter with epoxy resin. To prepare the filter, the crystals were cut into 5-cm diam cylindrical rods using a diamond core drill cooled with an aqueous solution nearly saturated with $NiSO_4 \cdot 6H_2O$. If the cores were oriented perpendicular to the (001) plane, they could be cleaved readily to provide disks of any desired thickness. 5.0-mm thick samples were used along with 4.0-mm Ultrasil disks and 9863 disks of various thicknesses to form the completed filter. A commercial Corning ultraviolet filter, No. 7-54, consisting of 9863 glass polished to a stock thickness of 3.0 ± 0.1 mm was also used in the measurements.

The absolute reflectometer in which the ultraviolet filters were used has been described previously.[9] It was designed for the infrared region of the spectrum and can be used to obtain specular reflectance values which are good to ±0.001. By substituting a tungsten source and multiplier phototube for the globar and thermocouple, the instrument also can be used easily in the visible and near-ultraviolet regions. However, at shorter-ultraviolet wavelengths its use is complicated by the large reflectance loss from the thirty or more reflections in the optical train. Wide slits and intense sources must be used, and scattered light in the instrument is, therefore, more critical than would be the case for most ultraviolet instruments. The Perkin-Elmer Model 99 monochromator used in this instrument is a single-beam, double-pass system in which the radiation is chopped between the first and second pass. This procedure is very efficient in modulating only radiation at the desired wavelength,[10] but since the system is not a double monochromator, considerable unmodulated, stray radiation falls on the exit slit. An unmodulated, single-pass image of the entrance slit having a slightly longer wavelength than that of the desired radiation also falls on the exit slit. However, since the slit image is inverted on each pass, the single-pass image is easily removed by masking half the height of the entrance and exit slits.

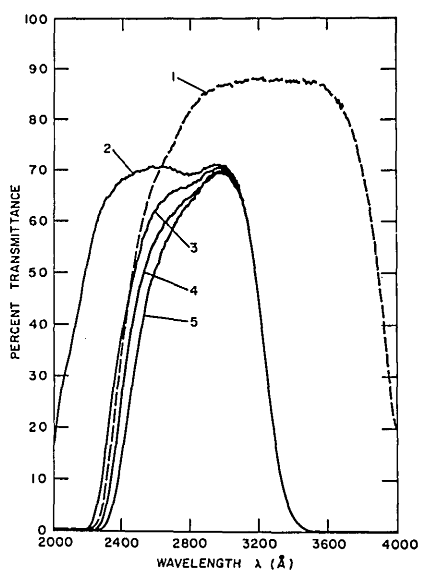

Fig. 1. Ultraviolet transmittance of various filters: (1) Corning filter 7-54, (2) 5.0-mm $NiSO_4 \cdot 6H_2O$ enclosed in two 4.0-mm Ultrasil disks, (3) 5.0-mm $NiSO_4 \cdot 6H_2O$ enclosed in 1.02-mm 9863 glass and 4.0-mm Ultrasil disks, (4) 5.0-mm $NiSO_4 \cdot 6H_2O$ enclosed in two 1.02-mm 9863 glass disks, (5) 5.0-mm $NiSO_4 \cdot 6H_2O$ enclosed in 3.05-mm 9863 glass and 4.0-mm Ultrasil disks.

The ultraviolet filter was mounted behind the exit slit, rather than in front of the entrance slit. This procedure is good practice when working in the ultraviolet since a marked decrease in transmission can occur in some filters which are exposed to intense ultraviolet radiation.[11] A xenon or mercury–xenon arc* was used as a source for the far-ultraviolet measurements. Such sources have considerably more energy in the ultraviolet than do the conventional hydrogen arcs, although they are usually not used as sources for ultraviolet instruments because of their intense, visible radiation. If they are operated under the conditions recommended by the manufacturer, they are sufficiently stable and noise-free for accurate photometric measurements. The detector was a DuMont type of 7664 multiplier phototube,† a kn-stage, 5.08-cm diam tube with S-13 response and silver–magnesium dynodes. In our experience this tube has proved to be stable, linear, and noise-free.‡

Results and Conclusions

The ultraviolet transmittance of the various filters used is given in Fig. 1. Figure 2 shows the transmittance of these filters in the visible and near-ultraviolet regions where opacity is desired. In order to determine the very small transmittances shown in Fig. 2, screens were used in the reference beams of Cary Models 11 and 14 spectrophotometers to reduce the reference level by a known amount. Curve 1 in Figs. 1 and 2 shows the transmittance of the No. 7-54 Corning filter which was used. The manufacturer monitors the transmittance of this type of filter to obtain a value of 40% or more at 2540 Å. Nominally the filter should have a transmittance of 10% at 4000 Å and 0.01% at 5000 Å, although variations in different filters from 0.03% to 0.004% at the latter wavelength have been observed. When working at wavelengths longer than 3000 Å, a No. 7-54 filter was sufficient to reduce the scattered light in the reflectometer to an acceptable level. However, at shorter wavelengths, near-ultraviolet filtering was necessary.

The transmission of a 5.0-mm thick, $NiSO_4 \cdot 6H_2O$ crystal encased in Ultrasil is shown in curve 2 of Figs. 1 and 2. Although this material absorbs strongly in the near ultraviolet and has good far-ultraviolet transmission, it does have a weak transmission band

* Obtained from Hanovia Chemical and Manufacturing Company, Newark, New Jersey.

† Obtained from the Allen B. DuMont Laboratories, Inc., Clifton, New Jersey.

‡ In accurate photometric applications, the choice of the multiplier phototube is critical. For example, several RCA-type 6903 tubes, which have a similar response, were tried but did not give results which were reproducible to three significant figures.

in the visible region centered at about 5000 Å. When this filter was used for far-ultraviolet measurements with the reflectometer, the scattered-light intensity in the visible region was sufficient to saturate the detector. Therefore, combination filters incorporating various thicknesses of Corning 9863 glass, together with the $NiSO_4 \cdot 6H_2O$, were used to determine what absorption was necessary in the visible region to reduce the scattered light to an acceptable level. Curves 3, 4, and 5 show the transmittances of filters employing 1.02-, 2.04-, and 3.05-mm thicknesses of 9863 glass, respectively. When these filters were tried in the reflectometer, wavelength regions could be found in which the less strongly absorbing filters could be used, indicating that the intensity of scattered light was strongly dependent on the wavelength setting of the monochromator. However, in order to eliminate all excessive noise in the signal over the entire 2400–3000 Å wavelength region, it was necessary to use the thickest piece of 9863 glass (curve 5). This filter transmits less than 0.01% in the visible region of the spectrum. A record of the signal from the mercury–xenon arc obtained using this filter is shown in Fig. 3(a). For comparison, a record run under the same conditions, using the Corning 7-54 filter, is shown in Fig. 3(b). The increase in noise level in the lower record is striking.

The necessity of incorporating Corning 9863 glass in the filter to give adequate absorbance in the 4500–5000 Å region seriously limits the short-wavelength transmission of the combination filter. Since the short-wavelength cutoff of the Corning glass varies from melt to melt, the use of selected batch materials and an investigation of melting techniques is under-

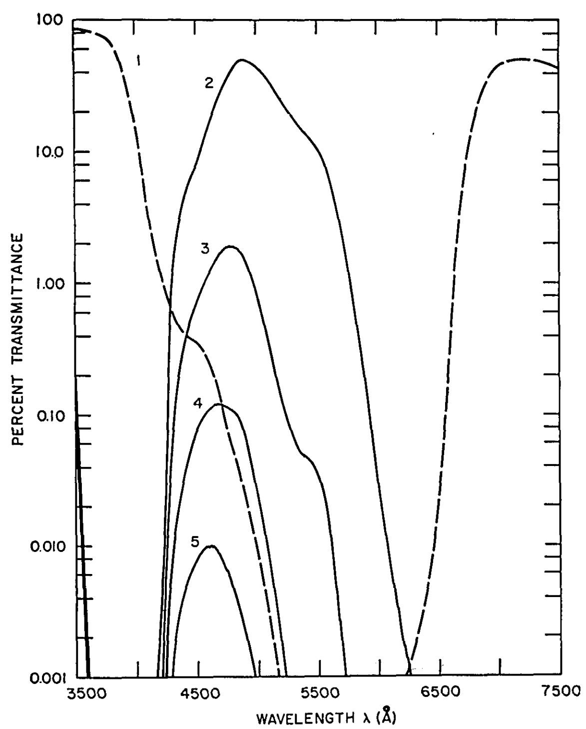

Fig. 2. Visible and near-ultraviolet transmittance of the filters shown in Fig. 1.

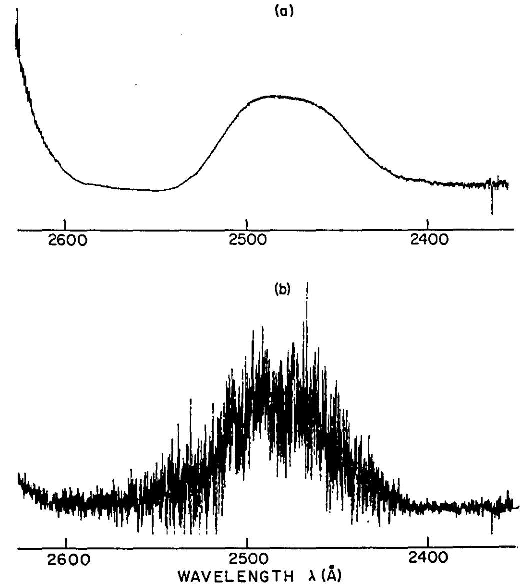

Fig. 3. Comparison of the signal from the mercury–xenon arc obtained with (a) filter 5, $NiSO_4 \cdot 6H_2O$ plus 9863 glass and Ultrasil, and (b) Corning 7-54 filter.

way.[12] The use of some other material such as an alkali halide with strong *F* center or metal-colloid absorption in place of the Corning glass has also been investigated.[5] Even with the present filters, however, it is possible, by using an intense source and filtering out the scattered light in the visible and near ultraviolet regions, to extend the range of instruments having large numbers of mirror reflections into the far ultraviolet without making modifications which would impair the versatility of the instruments at longer wavelengths.

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