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Raman Tube Filters

GEO. GLOCKLER AND JOHN F. HASKIN⁽¹⁾

A method for the application of plastic filter dopes to Raman tubes was developed. Such filters were devised for isolation of the 4358 Å mercury triplet, which was used as the exciting source. Derivatives of nitrobenzene dissolved in a urea-melamine-formaldehyde resin effectively removed the 4047 Å pair. During long exposures to mercury lamp radiations, these filters darkened. A film of light stable Eastman Acetate Lacquer 390-37-2 served the same purpose. Removal of continuous background was effected by Rhodamine 5GDN Extra in polymethyl methacrylate, Tygon lacquers, cellulose acetate, cellophane, or urea-melamine-formaldehyde resins. An Eastman gelatin filter produced similar results. A filter utilizing both the Eastman Acetate Lacquer and the Rhodamine dye in the urea-melamine-formaldehyde resin was stable to over 240 hours exposure to twelve General Electric A-H2 mercury lamps.

INTRODUCTION

The employment of various Raman tube filters in conjunction with mercury arcs furnishes one of the most practical monochromatic excitation sources. Selection of the particular exciting line is usually determined by the photodecomposition, fluorescence, and absorption characteristics of the scattering material. For most colorless substances, the intense 4358 Å mercury triplet is satisfactory. Moreover, it produces frequency shifts in a region of superior photographic sensitivity and relatively high dispersion for prism spectrographs. In order to minimize obscurity of Raman lines it is frequently necessary to remove the continuous background on the long wave length side of 4358 Å. The overlapping of the lines excited by 4047 Å on those produced by 4358 Å may be reduced by the diminution of the former.

A review of the research in the Raman field shows that, except for a number of standard glass filters, liquid filter solutions generally have been utilized. Venkateswaran (2) removed 4047 Å with freshly prepared quinine sulfate solution. A blue glass diminished the continuum. It has also been reduced by aqueous solutions of various rare earth salts (3, 4). More satisfactory 4047 Å filters were devised by High and Pool (5) who employed m-dinitrobenzene, and and by Pfund (6), with aqueous sodium nitrite. Sannie, Amy, and

1. Submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Department of Chemistry and Chemical Engineering, in the Graduate College of the State University of Iowa.
2. S. Venkateswaran, *Indian J. Phys.* 3, 105 (1928).
3. P. Krishnamurti, *Indian J. Phys.* 5, 1 (1930).
4. R. W. Wood, *Phys. Rev.* 36, 1421 (1930).
5. M. E. High and M. L. Pool, *Phys. Rev.* 38, 374 (1931).
6. A. H. Pfund *Phys. Rev.* 42, 581 (1932).

Paremsky (7) have studied several materials, including nitrobenzene and Rhodamine 5G Extra in alcohol, for the reduction of 4047 A and the continuous background respectively. Their procedure was modified by Edsall and Wilson (8), who employed an alcohol solution which contained two per cent of p-nitrotoluene and one part in 50,000 of Rhodamine 5GDN Extra (DuPont). Crawford and Horwitz (9) replaced the p-nitrotoluene by a Wratten 2A filter.

Apparently, the liquid materials frequently have a sharper cutoff and a greater transmission than is characteristic of glass filters. On the other hand, it is usually desirable to employ more than one filter material in the isolation of 4358 A. Since these different substances may be incompatible, or one or the other may undergo rapid decomposition, it is often necessary that the solutions be separate.

In order to reduce the number of reflecting surfaces and complicated filter solution jackets, plastic filter dopes (10) were applied directly on the Raman tube or on the inside of a glass cylinder, which may surround the former.

METHODS OF APPLICATION

The Raman apparatus described by Glockler and Tung (11) was employed. It utilizes two horizontal Raman tubes, one mounted above the other, inside a circular arrangement of twelve General Electric A-H2 mercury lamps. One tube is supplied with a filter, and the other used as a standard. Exposures are simultaneous. Obviously, cylindrical filters are desirable.

With a suitable method for incorporating the various dyes into the molding powders, satisfactory molded filters might have been obtained. However, it was found more convenient to dissolve the absorbing materials in partially polymerized plastic dope, or in molding powder solutions. Cylindrical filters were produced by centrifugal casting on the inside of a two-inch glass tube. The latter was mounted on two rubber stoppers. Passing through the center holes of the stoppers was a $\frac{1}{4}$ inch steel shaft, fitted with suitable bearings and driven by a variable speed motor, as shown in Figure 1. The desired amount of dope was poured into the cylinder, and the motor started. Solvent evaporation was facilitated by auxiliary holes in the stoppers, through which an air blast was directed.

However, an entirely different method of procedure was invented which consisted in the direct application of plastic films to the Raman tube. This approach to the problem turned out to be much

7. C. Sannie, L. Amy, and V. Paremsky, *Bull. Soc. Chim. France* 3, 2018 (1936).
8. J. T. Edsall and E. B. Wilson, Jr., *J. Chem. Phys.* 6, 124, (1938).
9. Bryce L. Crawford, Jr., and William Horwitz, *J. Chem. Phys.* 15, 268 (1947).
10. George Glockler and John Haskin, *J. Chem. Phys.* 15, 759 (1947).
11. Geo. Glockler and Jo-Yun Tung, *J. Chem. Phys.* 15, 112 (1947).

more satisfactory than any other scheme tried. The tube was dipped vertically into a plastic solution. Having been slowly and evenly withdrawn from the liquid, it was permitted to drain vertically for

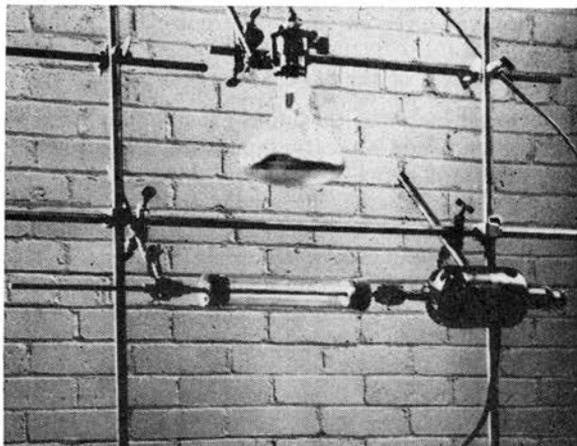


Figure 1. Centrifugal casting apparatus. The desired amount of plastic dope is introduced into the tube, and a film is cast on the inside.

a few seconds, and was then attached to the rotating drying spindle, illustrated in Figure 2. Two two-hole rubber stoppers were mounted on the shaft, about three inches apart. The filler neck of the

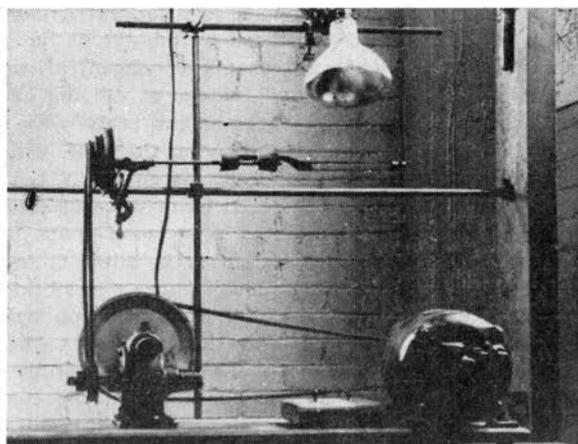


Figure 2. Rotating drying spindle with infrared lamp.

Raman tube was then fitted through the other holes of the stoppers. This arrangement provided an offset so that the center of the tube coincided approximately with the axis of rotation. By means of a

straddle-mounted pulley, the spindle shaft was driven at a rate of approximately 12 R. P. M. The pulley drive was supplied through a worm reduction gear. At this rate of rotation smooth films were obtained, and the material was not thrown off the tube. Heat from an infrared lamp was directed on the thermosetting resins.

Filters for the Remocal of the 4047 A Mercury Line.

Generally characteristic of the nitro group is an absorption band in the 4050 A region and an extension toward the ultraviolet. The transmission increases between 4050 and 4400 A and remains high throughout the visible. The sharpness and exact position of the cut-off varies with the radical to which the nitrogen is attached. However, materials as dissimilar as p-chloronitrobenzene and the nitrite ion both produce satisfactory results.

In their plastic infrared filters, Shenk et al (12) used Melmac 599-8 (an alkyd modified melamine-formaldehyde resin, American Cyanamid Co.) and Beetle 230-8 (an unmodified urea-melamine-formaldehyde resin from the same manufacturer). The Beetle films gave better transmission in the visible (88-92 per cent), and therefore were employed in this research. p-nitrotoluene in Beetle films produced the desired cutoff, but indicated a marked tendency to sublime in the resin curing process. m-dinitrobenzene did not offer this difficulty, but its low solubility in the resin necessitated excessively thick films for the proper absorption.

p-chloronitrobenzene is more satisfactory. A suitable dope consists of 78 per cent Beetle, 15 per cent p-chloronitrobenzene, 5 per cent castor oil, and 2 per cent Beckamine P-198 accelerator (Reichhold Chemicals, Inc.). The proportions are not extremely critical, and the castor oil is frequently replaced by dibutyl phthalate. However, an increase in the p-chloronitrobenzene concentration resulted in crystallization and "crawling out." Instead of dipping the Raman tube in the plastic, it was found that thicker coats were obtained by actually pouring an excess of the dope on the tube, while it was rotating on the horizontal spindle drier. After about ten minutes of air drying, the rays from an infrared lamp were directed on the film for a period of 20 to 30 minutes. Five such coats produce a 1.2 mm layer. The original transmission of the filter is represented by the upper curve in Figure 3. The lower curve was obtained after the film had been exposed 44 hours in the spectrograph light chamber. Unfortunately, this photodecomposition appears to be characteristic of all the nitro compounds which have been studied in this investigation. A spectrum of benzene contained in the coated tube indicates that no Raman lines are excited by the 4047-4078 A pair, although the latter faintly appear.

Another filter dope investigated was composed of 0.1 g p-nitroaniline in 50 g Tygon TP-81 N (a vinyl acetate-vinyl chloride lacquer

12. John H. Shenk, Edwin S. Hodge, Robert J. Morris, Edward E. Pickett, and Wallace R. Brode, *J. Opt. Soc. Am.* **36**, 569 (1946).

manufactured by U. S. Stoneware Corp.). The region 4047-4078 Å was effectively removed, and about 74 per cent of 4358 Å was transmitted by a 0.05 mm film. However, it dropped to 22 per cent after

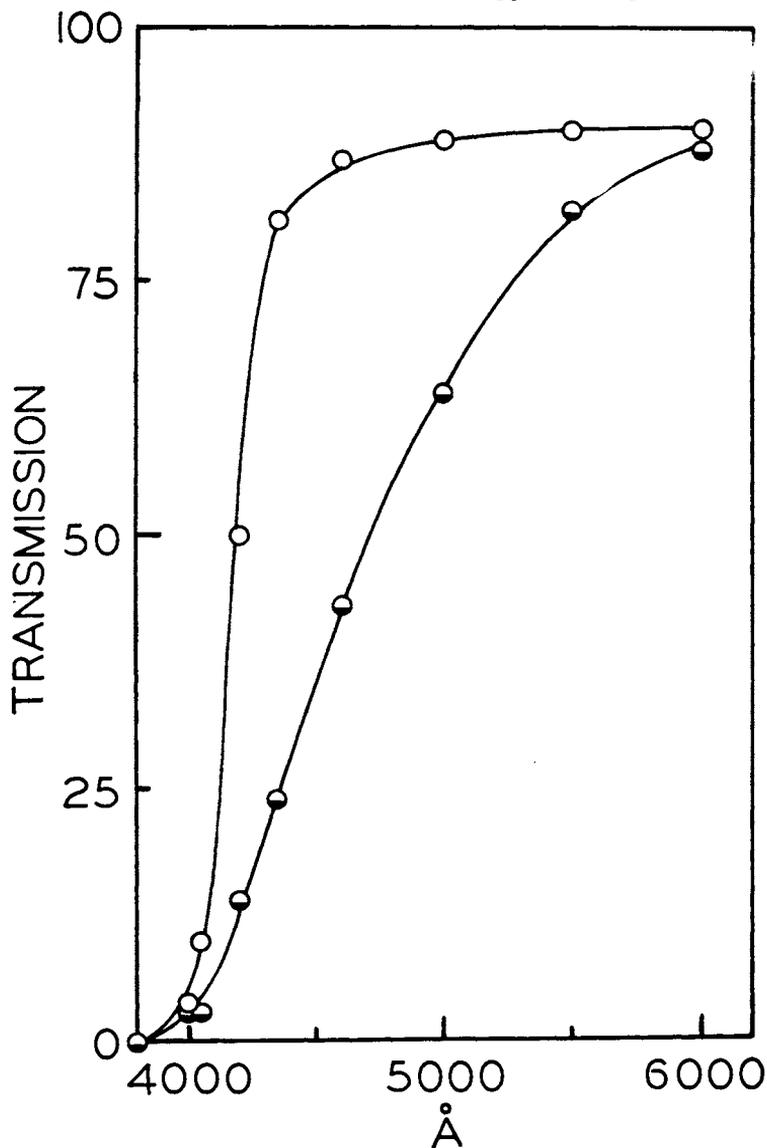


Figure 3. Decomposition of p-chloronitrobenzene filter. The upper curve shows the transmission of a 1.2 mm film of Beetle resin which contained 15 per cent of p-chloronitrobenzene. The lower curve was obtained after the film had been subjected to the mercury lamp radiations for 44 hours.

15 hours exposure to the twelve mercury lamps. Pickett (13) has used cellophane in a similar filter.

An excellent stable 4047 Å filter is produced by an 0.08 mm film

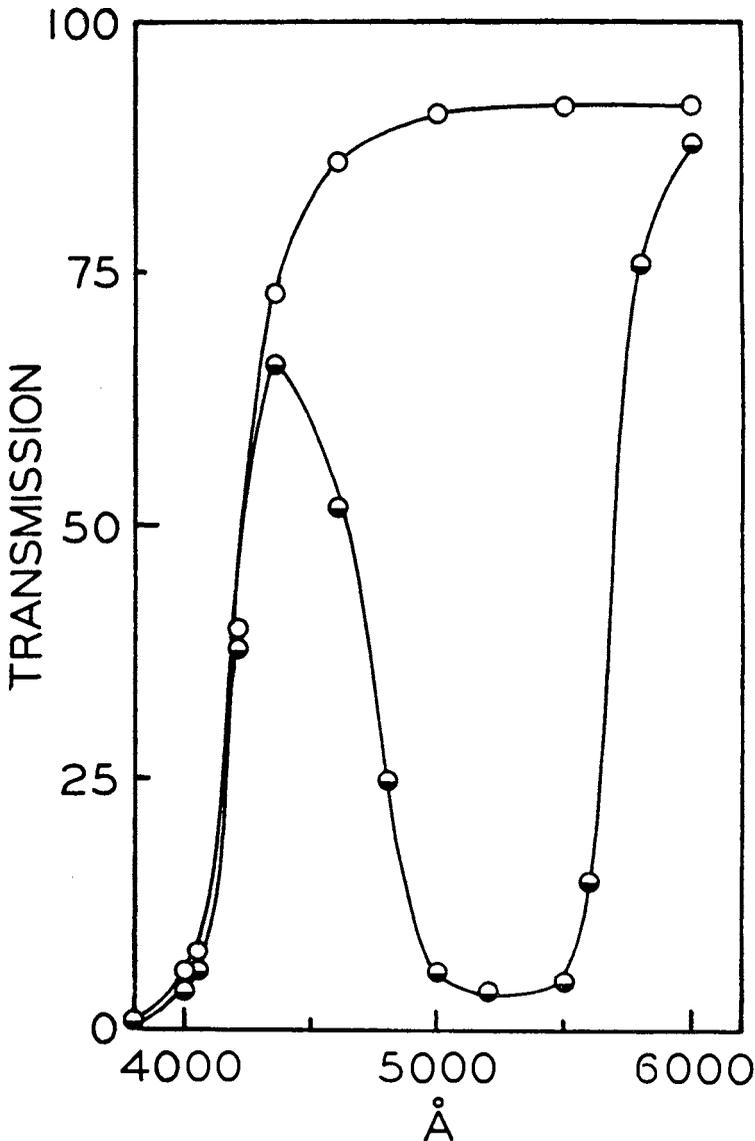


Figure 4. Upper curve—Transmission of an 0.08 mm film of Eastman Acetate Lacquer 390-37-2. Lower curve—Same filter with a 0.22 mm layer of Rhodamine-Beetle dope.

13. Edward E. Pickett, Private communication.

of Eastman Acetate Lacquer 390-37-2. This material was furnished by Dr. E. M. Lowry of the Eastman Physics Division. It was applied by dipping the Raman tube, and drying it on the rotating spindle. The thickness of the film is regulated by the viscosity of the dope. A mixture, composed of 40 g acetone, 10 g ethyl lactate, 10 g ethyl acetate, and 10 g toluene serves as a satisfactory thinner. The transmission of this film is indicated by the upper curve in Figure 4. Exposures totaling over 240 hours effect no change.

Filters for Removal of the Continuous Background.

Because of its desirable optical properties, polymethyl methacrylate was the first medium considered. With a suitable method of incorporating the various dyes into the molding powder, satisfactory compression-molded filters might have been obtained. However, it was found more convenient to dissolve the absorbing material and the methyl methacrylate powder in a solvent. A suitable dope was composed of 70 mg Rhodamine 5GDN Extra and 34 g polymethyl methacrylate dissolved in 200 ml glacial acetic acid and 60 ml acetic anhydride. Three coats were applied to the Raman tube by the usual dipping procedure. A two-hour exposure of benzene contained in the tube produced a clear Raman spectrum, while the one obtained without a filter scattered a continuous background which obscured the lines. The filter was light stable.

A solution of 10 g Dow PS-65 polystyrene molding powder dissolved in 20 g xylene produced films with excellent optical properties, but none of the dyes considered in this research were sufficiently soluble in the dope.

The Rhodamine dye which was used to reduce the continuous background is unstable in Tygon TP-81 N. It is evidently decomposed by the traces of hydrogen chloride and chlorine released from the chlorinated hydrocarbon solvents under the intense illumination. A different type of the lacquer, Tygon TP-81, did not decompose the dye. However, the solubility of Rhodamine in this dope is somewhat limited. A fairly suitable mixture contained 0.1 g Rhodamine 5GDN Extra in 100 g of the lacquer.

A simple and economical resin was formulated from a solvent mixture and discarded Kodak safety X-ray films. It contained 40 g acetone, 10 g ethyl acetate, 10 g ethyl lactate, 10 g toluene, and 15 g of safety film from which the emulsion was removed. To 25 ml. of the stock lacquer, .05 g Rhodamine 5GDN Extra was added. A .02 mm film reduced the background, and transmitted 75 per cent of 4358 Å. However, the value dropped to 56 per cent after a 72 hour exposure.

Cellophane is a practical light filter base. If ordinary wrapping cellophane is soaked in water for about five minutes, the lacquer may readily be removed. After it has been peeled off) the film is wrapped around a Raman tube submerged in water. Air bubbles are thereby eliminated. The coated tube is dried for an hour, and

then dipped in aqueous Rhodamine 5GDN Extra solution which contains 25 per cent ethanol and enough of the dye to give a deep tint. Although this procedure is not very systematic, some satisfactory filters were obtained.

An Eastman X-3225 film type filter wrapped around the Raman tube absorbs the continuous background. The transmission is quite similar to that of the Rhodamine filters. It is light stable.

The Beetle resin used in the 4047 A filters, is quite satisfactory as a medium for filters of this type also. One mixture contained 186 g Beetle, 10 g dibutylphthalate, 4 ml Beckamine P-198, and 0.2 g Rhodamine 5GDN Extra. The transmission of a 0.4 mm film, illustrated in Figure 5, remained unchanged after 240 hours.

Another filter of this type employed Gentian Violet. The plastic dope was identical to that of the previous filter. However, the Rhodamine was replaced by 0.3 g Gentian Violet. Although the cutoff beyond 4358 A was somewhat sharper than that observed in the Rhodamine filters, a 48 hour exposure reduced the 4358 A transmission from 73 to 31 per cent.

Any of the Beetle dopes mentioned here may be applied directly to the Raman tube. Bubble formation in the films may become objectionable. Sometimes they can be eliminated from the freshly applied film by a few drops of acetone. However, it is better to avoid stirring the mixture immediately before application. The resins which contain Beckamine P-198 accelerator are best kept in a refrigerator. Otherwise, the dope jells in warm weather.

CONCLUSIONS

The pair of mercury lines 4047 and 4078 A is removed satisfactorily by nitrobenzene derivatives in Beetle, while the 4358 A line is transmitted sufficiently. Since the absorption per molecule of such compounds is evidently rather small, and their solubilities in the resins are low, relatively thick films were necessary. Only the Beetle resin offered good compatibility and could be applied in several thick coats. However, only thin coats of the light stable Eastman Acetate Lacquer were required to produce similar transmission.

The continuous background from 4400 A to 5800 A is suppressed by Rhodamine 5GDN Extra in any one of the several plastics tested in this investigation. In order to remove both 4047 and 4078 A lines and the continuous background, a combination filter was devised. An .08 mm film of Eastman Acetate Lacquer 390-37-2 was applied directly to the Raman tube. On top of this coat was a 0.22 mm layer of the Beetle-Rhodamine dope mentioned above. The transmission is given in the lower curve of Figure 4. Exposures totaling over 240 hours produced no significant change. Figure 6 illustrates two Raman spectra of benzene. The top tube was coated with the two filter materials, while the middle spectrum was scattered by benzene in the uncoated tube. A mercury spectrum, with the 4358 A triplet to the right of the center, may be seen at the bottom. The

4916 Å mercury line at the right is removed by the filter. The Raman lines excited by the 4047 and 4078 Å mercury pair, which appears in the middle spectrum, do not appear in the top spectrum.

These films are comparable to liquid filters. They offer the ad-

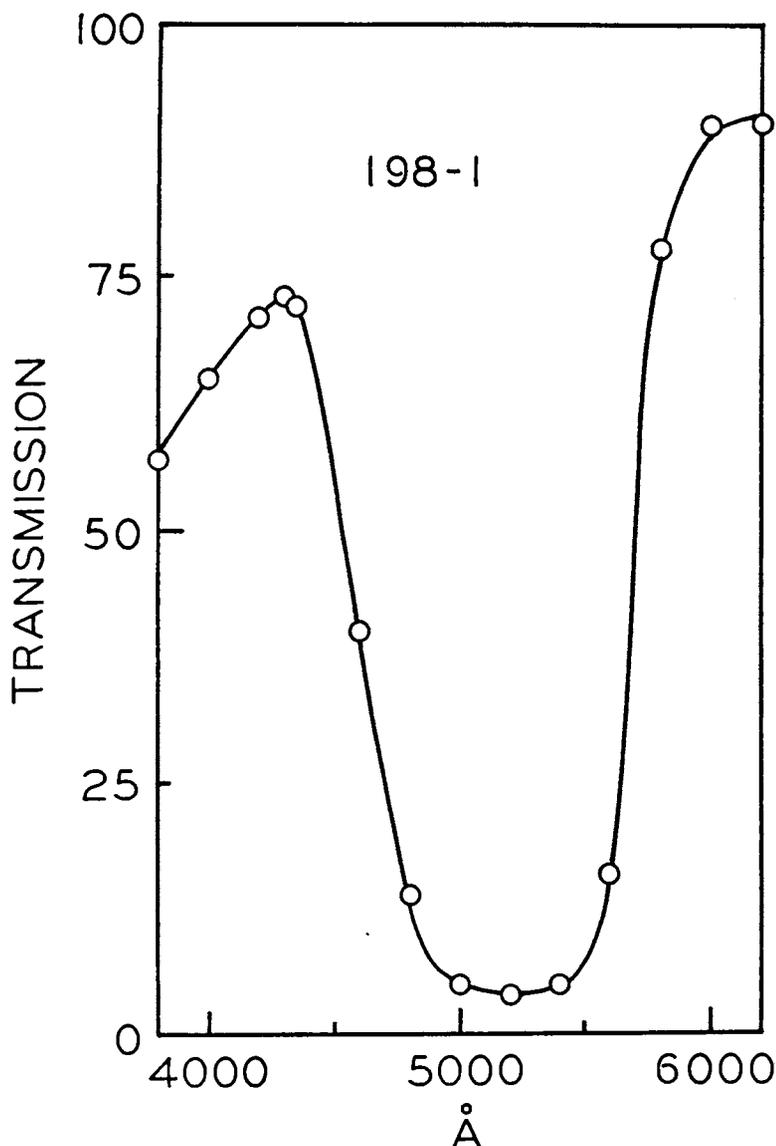


Figure 5. Transmission of Rhodamine-Beetle filter. The 0.4 mm film contained 0.2 g of Rhodamine 5GDN Extra in 186 g of Beetle resin.

vantages of apparatus simplification, convenience, and economy. In some cases the overall transmission is also greater.

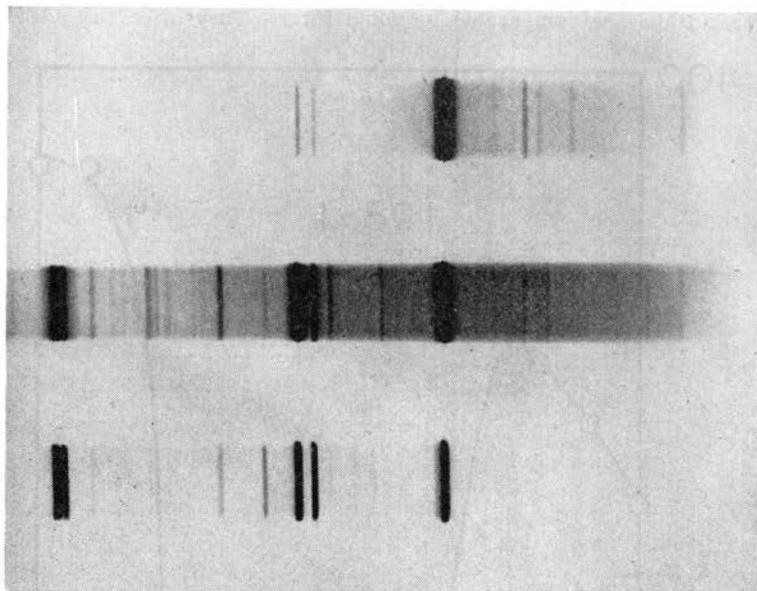


Figure 6. Raman spectra of benzene. (Simultaneous exposures). Top—tube coated with acetate and Rhodamine—Beetle filters. Middle—no filter. Raman lines excited by both 4047 A and 4358 A may be seen, partially obscured by the continuous background. Bottom—mercury spectrum.

ACKNOWLEDGEMENTS

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