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BY

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# AN INTEGRATING SPHERE COATING FOR THE VACUUM ULTRAVIOLET SPECTRAL REGION

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## Abstract

Integrating spheres are commonly coated with smoked magnesium oxide for use in the spectral region from 0.25 to 2.5 microns. The extension of these limits to higher and lower wavelengths has been hampered by the lack of suitable sphere coatings. There are several ways to overcome this coating problem and the solution proposed here utilizes the fluorescent properties of sodium salicylate to enable an integrating sphere to operate in the region from 500Å to 2000Å. The sphere is first coated with a magnesium oxide pigmented paint which is both durable and highly reflecting in the spectral region at which sodium salicylate fluoresces. This substrate is then overcoated with a thin layer of sodium salicylate which is sensitive to the radiation reflected by the sample. At the same time, the substrate-fluoresceor combination is a relatively good diffuse reflector of the incident fluorescent radiation. A description of the spectrophotometer employed for this investigation is given together with results of measurements made on some diffusely reflecting materials.

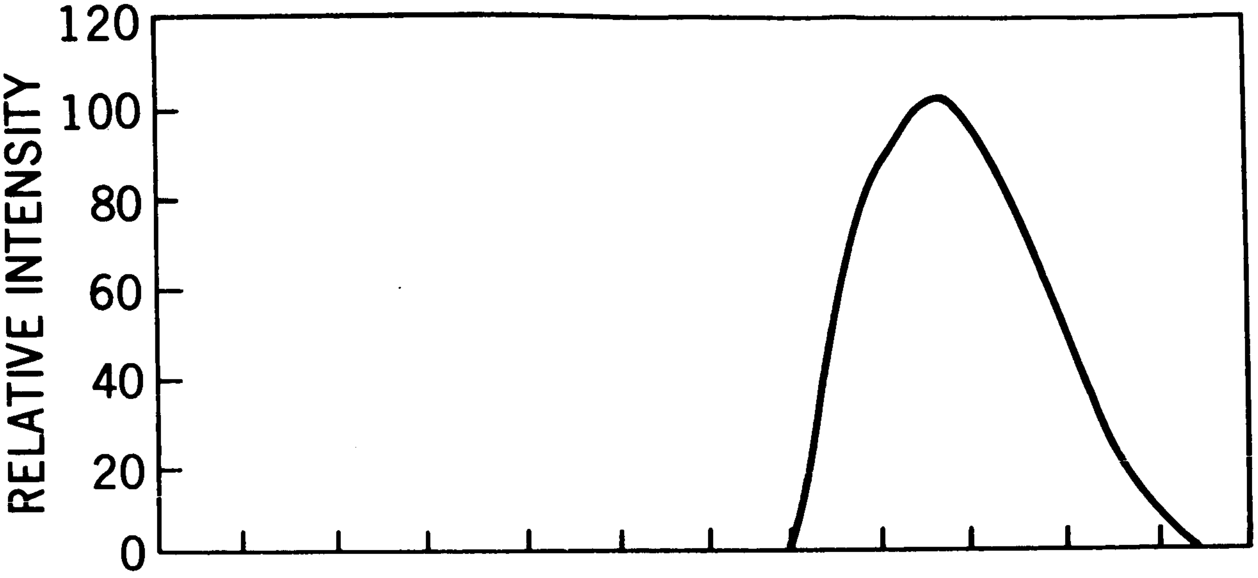
# AN INTEGRATING SPHERE COATING FOR THE VACUUM ULTRAVIOLET SPECTRAL REGION

## INTRODUCTION

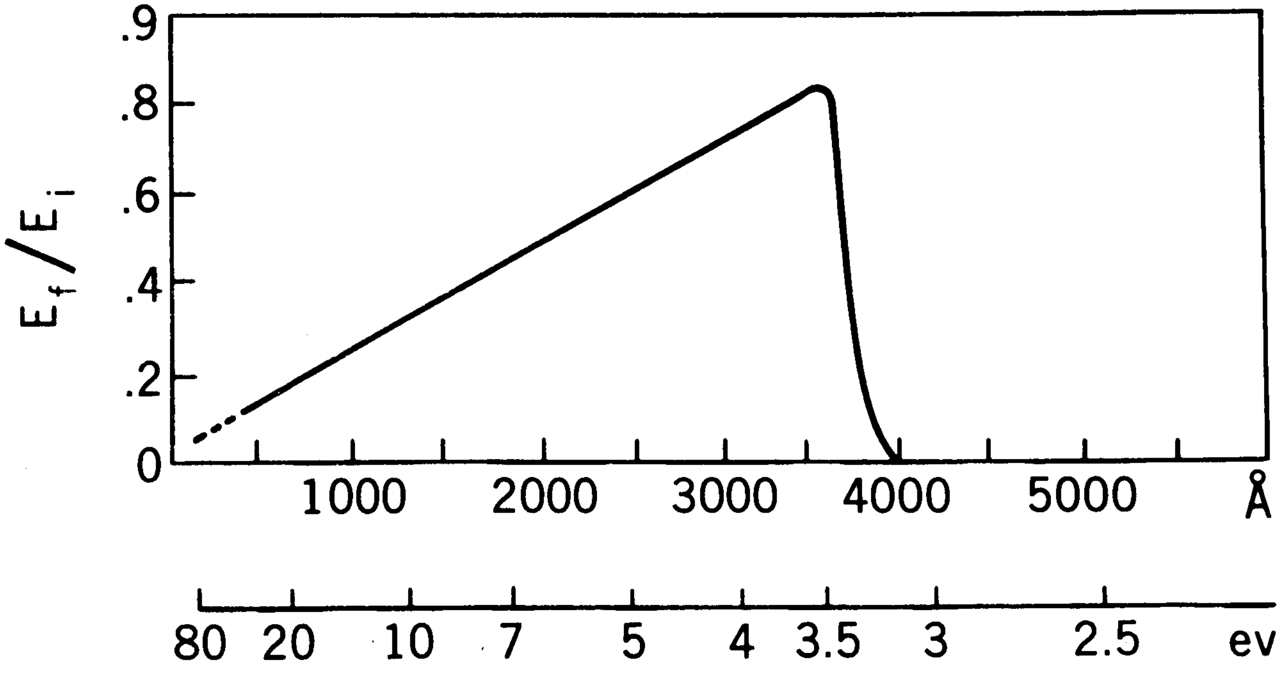
The measurement of total reflectance is commonly made in integrating sphere type reflectometers in which both specular and diffuse components of the reflected flux illuminate the sphere and consequently impinge upon the detector. The wavelength range over which this measurement can be made is primarily limited by the efficiency of the sphere coating, usually smoke deposited magnesium oxide, whose reflectance decreases rapidly below .25 microns and beyond 2.5 microns. In the lower regions of the ultraviolet, reflectance measurements are restricted to observing the specular component alone, or at best, a goniometric scan is made of the reflectance profile. These measurements are really inadequate when used to estimate the total reflectance of a diffusely reflecting material, such as a white paint. In order to include the diffusely reflected component, it would be desirable to construct an integrating sphere type reflectometer which would operate in the spectral region of interest, that is below 2000Å. The sphere wall coating should be sufficiently responsive to the incident radiation to guarantee an overall sphere efficiency great enough to overcome any signal to noise ratio problems in the detector electronics. This coating should also be a good diffuser and should exhibit a uniform sensitivity over the surface of the sphere. Sodium salicylate satisfies these requirements, if properly applied, and we can make use of its fluorescent properties to extend the operating range of the sphere down to at least 500Å.

## DEVELOPMENT

The use of sodium salicylate as an ultraviolet wavelength converter is widespread and its fluorescent properties have been thoroughly investigated. Its attractiveness as a wavelength converter stems primarily from the fact that its fluorescent yield is independent of the wavelength of the exciting radiation over a broad spectral band from 3600Å to at least 500Å.[1, 2, 3] In addition to this, the fluorescent radiation is contained in a band surrounding 4430Å which coincides with the wavelength of maximum sensitivity for a number of commonly available photomultipliers. Figure 1 is taken from a report by Krokowski[2] and is used here to demonstrate that the quantum efficiency of sodium salicylate is constant. Figure 1a is the spectral distribution of the fluorescence. In Figure 1b, $E_f$ over $E_i$ is the ratio of the energy of fluorescence to the incident exciting energy and corresponds to the energy conversion efficiency of sodium salicylate as a function of exciting wavelength. This leads directly to the conclusion that sodium salicylate has a constant quantum efficiency — at least over the wavelength region in which we are here interested. Figure 2 shows this relative quantum



A) FLUORESCENT SPECTRUM



B) ENERGY YIELD

Figure 1. The Fluorescent Spectrum and Energy Yield of Sodium Salicylate

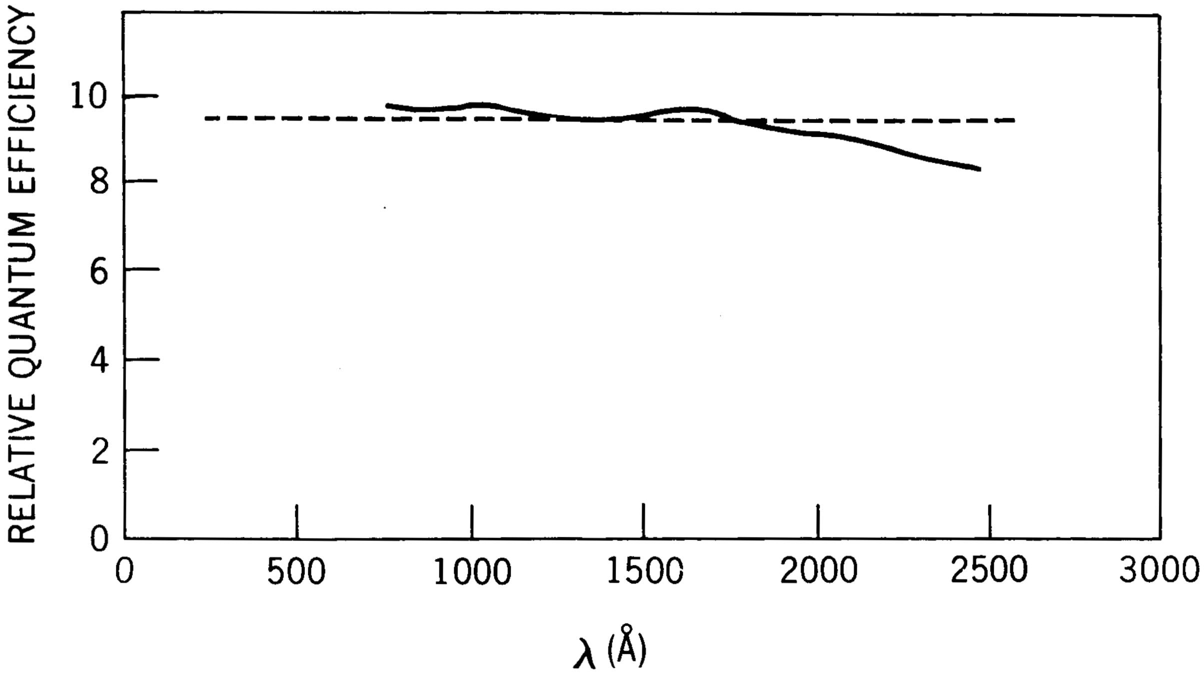


Figure 2. The Relative Quantum Efficiency of Sodium Salicylate

efficiency as a function of wavelength. For the application described in this report it is not necessary to know the absolute quantum efficiency of sodium salicylate. Figure 3 matches the fluorescent radiation band with the spectral response

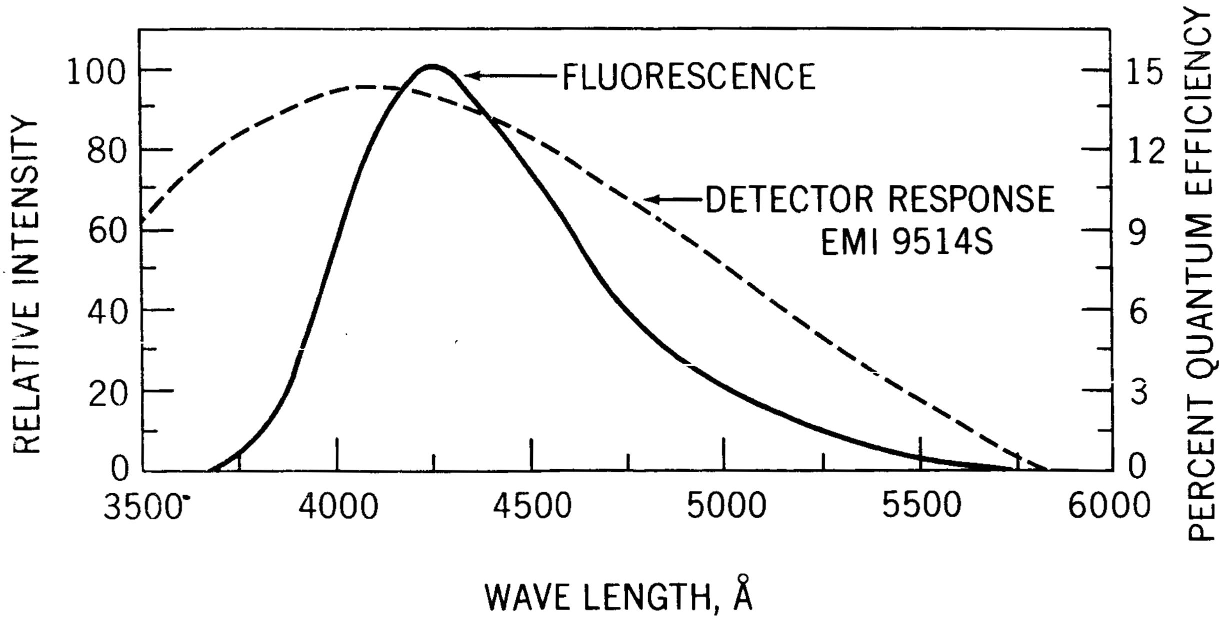


Figure 3. Comparison of Fluorescent Energy Band Width with Detector Response

data supplied with the photomultiplier used in this investigation, an EMI tube with an S type response.

An important parameter which should be considered next is the desired thickness of the sodium salicylate coating. This choice of thickness can determine the overall sensitivity of our coated sphere, as well as its uniform diffuseness. The coating is generally applied by spraying a solution of 31 mg/ml of sodium salicylate in acetone with a fine air brush onto a substrate, which in this case is a painted sphere wall. However, as long as we achieve a thickness somewhere between 1 and 3 mg/cm$^2$, we need not worry about having a nonuniform thickness. This can be seen from Figure 4 which presents the relative intensity of fluorescent radiation as a function of thickness, based on work done

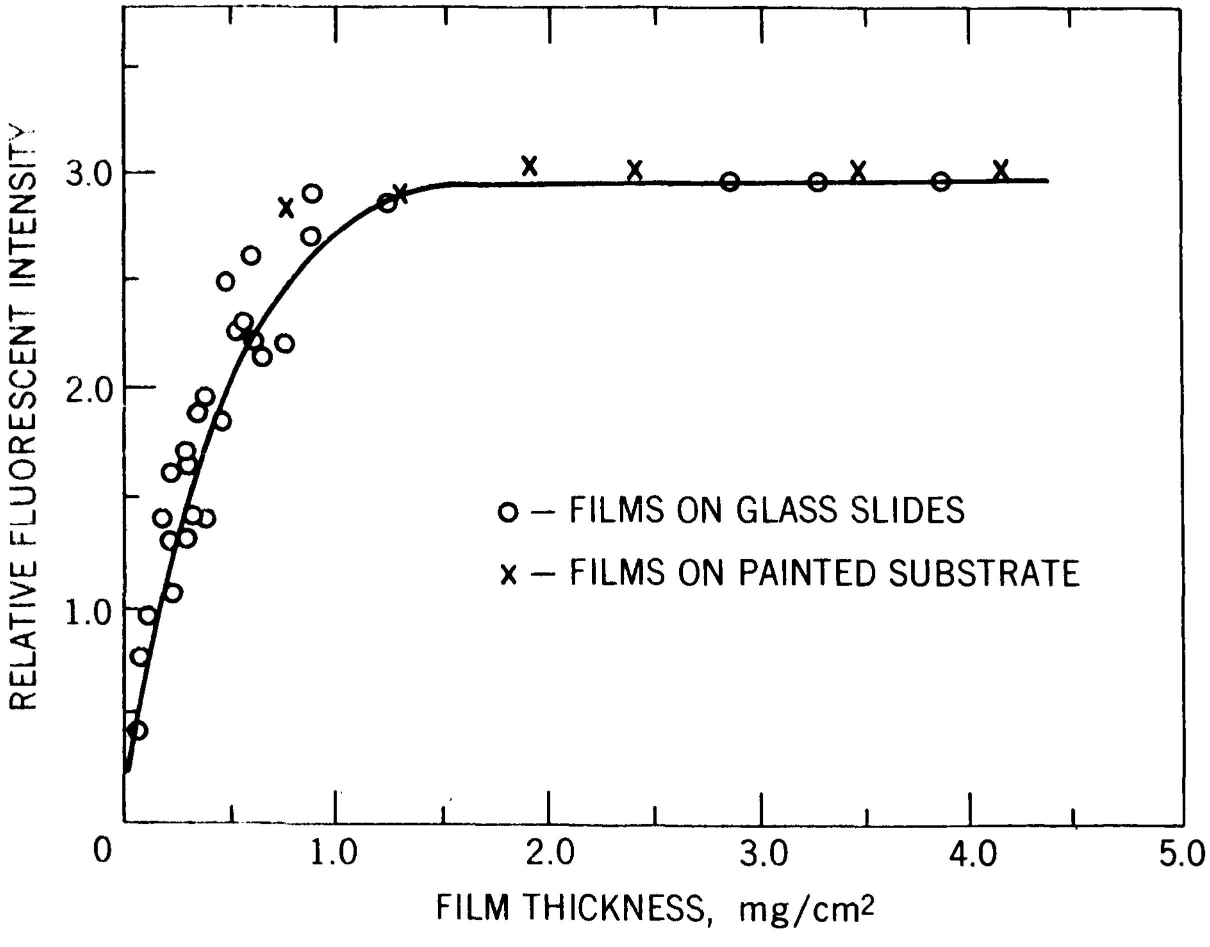


Figure 4. Fluorescent Intensity as a Function of Film Thickness for Two Types of Substrates

by Allison, et al.[4] This data was obtained from measurements made on sodium salicylate coated glass slides but preliminary measurements made on samples simulating the sphere wall agree well with the earlier data, as indicated by the points in Figure 4. The samples used were chosen to be close approximations to the actual sphere wall and they consisted of sodium salicylate deposited onto a magnesium oxide pigmented paint on an aluminum substrate. Radiation of 1216Å was incident on the samples at 45° and a portion of the resulting fluorescent flux was viewed by the detector. Thickness was determined by weighing before and after each coating application. From this we conclude that the intensity of fluorescent radiation coming from any point on the sphere wall should be independent of the thickness at that point.

The thickness of the sodium salicylate will play a large part in determining whether or not the sphere wall is uniformly diffuse. Figure 5 shows the angular

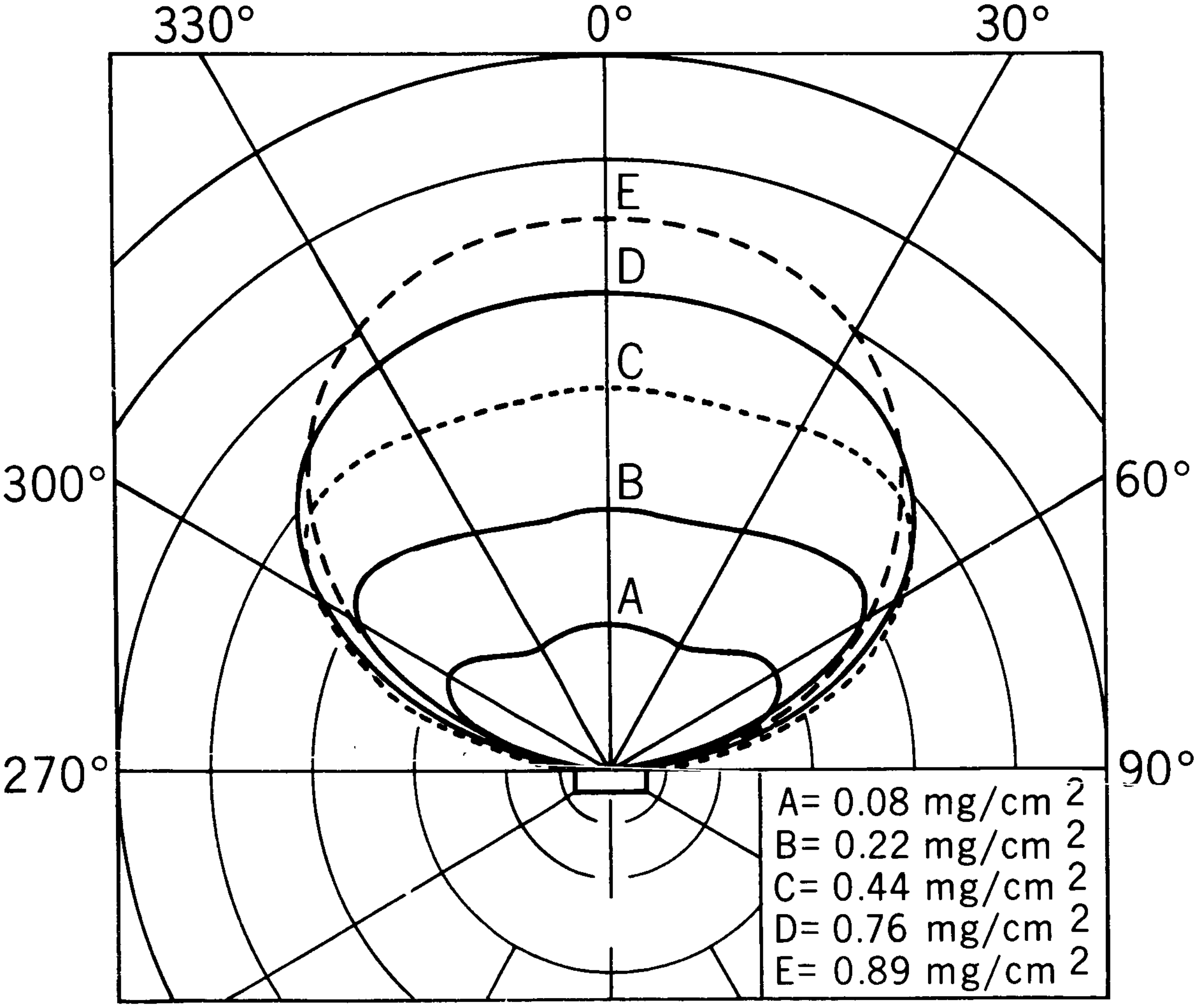


Figure 5. Angular Distribution of Fluorescent Radiation from Films of Sodium Salicylate of Various Thicknesses

distribution of fluorescent radiation as a function of film thickness as reported by Allison, et al.[4] This indicates that low ultraviolet radiation incident upon the sphere wall, will cause the sphere to be uniformly illuminated by the diffuse fluorescence. Then, in turn, this fluorescent radiation, with a wavelength of approximately 4400Å, will be diffusely reflected by the combined sodium salicylate and magnesium oxide paint, which is itself a good diffuse reflector as shown in Figure 6. This graph shows the ratio of the incident to the reflected flux, in arbitrary units, as a function of viewing angle for a magnesium oxide sample overcoated with sodium salicylate having a thickness of approximately 1.5 mg/cm$^2$. The incoming flux is radiation of 4300Å and is incident on the sample at 20°. From Figures 5 and 6 it is evident that the sphere will be diffusely illuminated by the exciting radiation that has been either speculary or diffusely reflected from a typical sample.

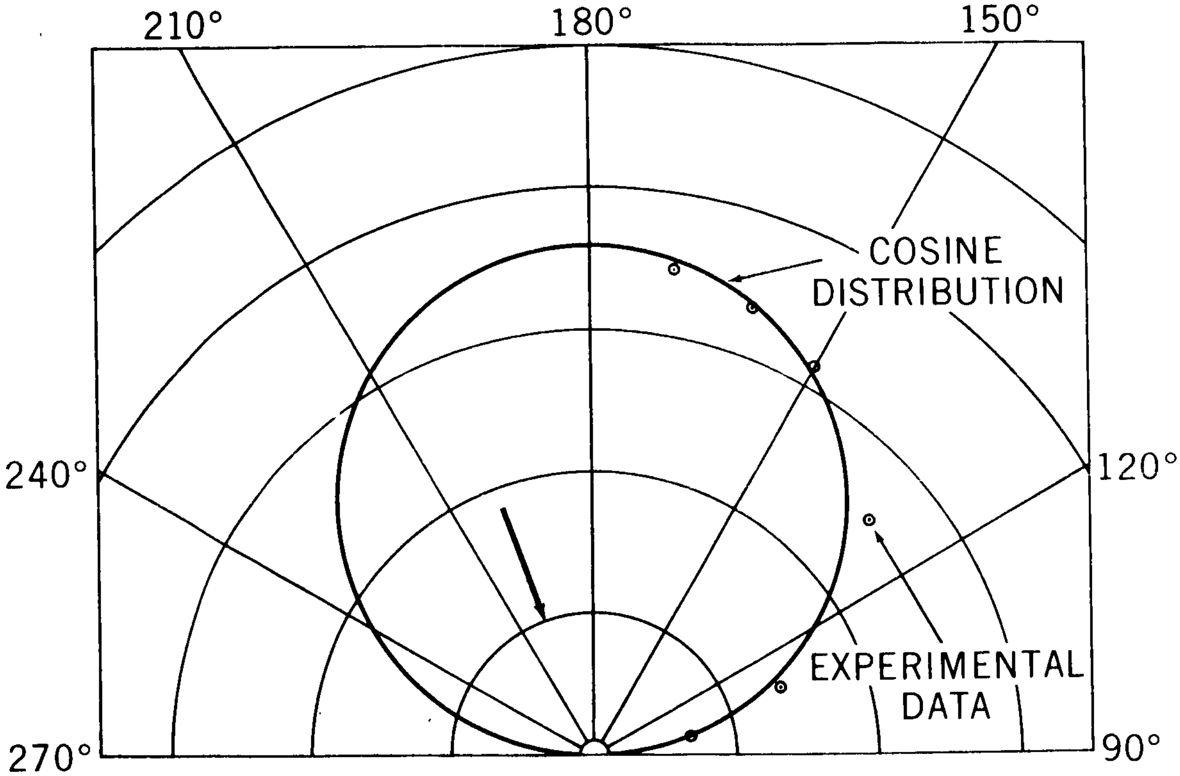


Figure 6. Angular Distribution of Radiation (4300Å) Incident at 20° and Reflected by a Sodium Salicylate Film 1.5 mg/cm$^2$ Thick Over Mg O Paint

Coating durability is important in integrating spheres and sodium salicylate, used as it is here, is in general durable in the sense that it will maintain a relatively high sensitivity months after application. Of course, care must be taken to avoid contaminating the film with such things as pump oil and the less time it spends in air, the longer it will retain its sensitivity. The stability of fluorescence as a function of time has been investigated, but it is too dependent on the system in which it is being used to make any generalizations other than to say that our experience has shown a slow decline in sensitivity over a period of months.

A survey of the above information presents us with the possibility of using sodium salicylate to coat the interior wall of an integrating sphere. Since films of sodium solicylate in the 1 to 3 mg/cm$^2$ thickness range are relatively transparent to the fluorescent radiation, it was decided to undercoat this film with a highly reflecting, diffuse substrate. At first, smoked magnesium oxide was used as the substrate, but this was replaced by a magnesium oxide pigmented white paint which worked equally well and had the advantage of being more rugged. Figure 7a shows the transmittance of sodium salicylate as a function of thickness in the wavelength region from 4000Å to 5000Å which includes most of the fluorescent radiation. Figure 7b shows the reflectance of the sodium salicylate — magnesium oxide paint combination for a given thickness in the same band. Because of this relatively low reflectance, we cannot expect the same sphere efficiency as that obtained from spheres operating exclusively in the so-called solar wavelength region. Nevertheless, the information indicated that such a sphere might sustain a signal strong enough to make reflectance measurements possible.

## INSTRUMENTATION

The operation of this integrating sphere can best be explained by examining Figure 8a which depicts a segment of the sphere surface enlarged for clarity. Incident low ultraviolet irradiation strikes the sodium salicylate coated sphere wall (either unreflected or reflected by some sample) and excites fluorescence. If the coating is sufficiently thick and properly uniform, almost all of the incident flux will initiate fluorescence in all directions. The fluorescent radiation, having a wavelength of approximately 4400Å, will, in the outward direction, be reflected by the magnesium oxide paint and returned to the sphere through the sodium salicylate coating. Radiation in the inward direction will be reflected by the sodium salicylate — magnesium oxide paint surface as shown in Figure 8b. The reflectance of this surface has been shown in Figure 7b. As a result, the sphere should be uniformly illuminated with radiation that can be detected.

It would be advisable to point out that the sphere described here was developed primarily to test the coating and not to make exact reflectance measurements per se. In the interests of expediency, time and cost, existing equipment was used whenever possible and therefore the design of this sphere may not be

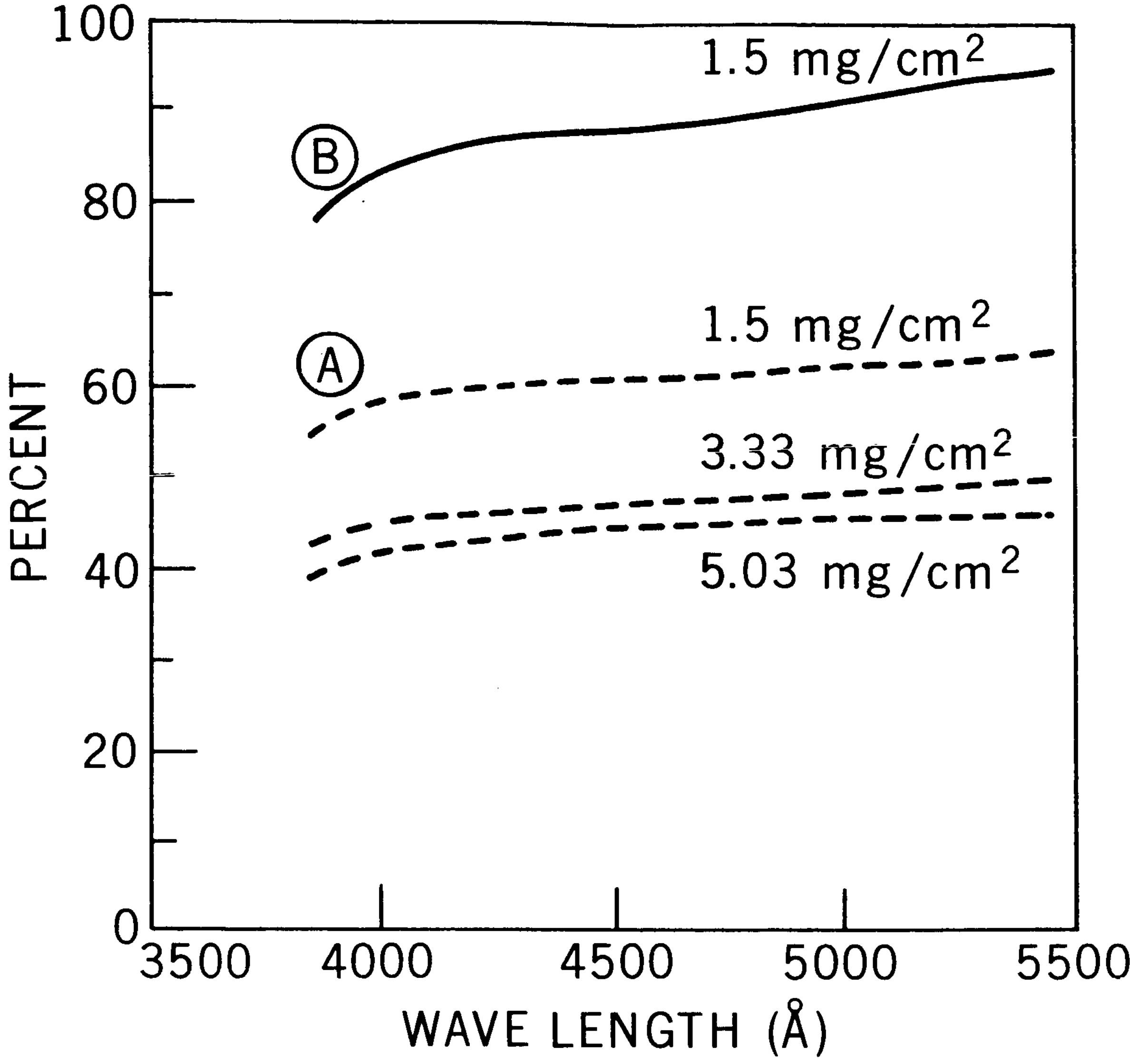


Figure 7. A. Transmittance of Thin Films of Sodium Salicylate
B. Reflectance of a Typical Sodium Salicylate Over Mg O Paint Sample

coincident with what is normally accepted as sound integrating sphere design. The primary limitation imposed upon the design of the sphere was the vacuum housing into which the sphere is placed during operation. The size of the photomultiplier comprised the second limitation. It was rather large for the sphere in question but its spectral response, sensitivity and availability made it attractive. A picture of the sphere and detector is shown in Figure 9. The sphere was spun in separate halves from sheet aluminum and overcoated with magnesium oxide paint as shown in Figure 10, together with the top segment that can be removed to permit the sample to enter. The small hole in this segment is for the

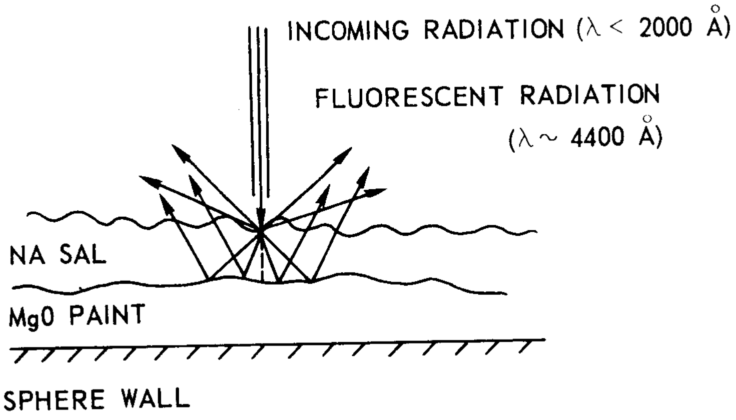


Figure 8a. Enlarged Cross Section of the Coated Sphere Wall.

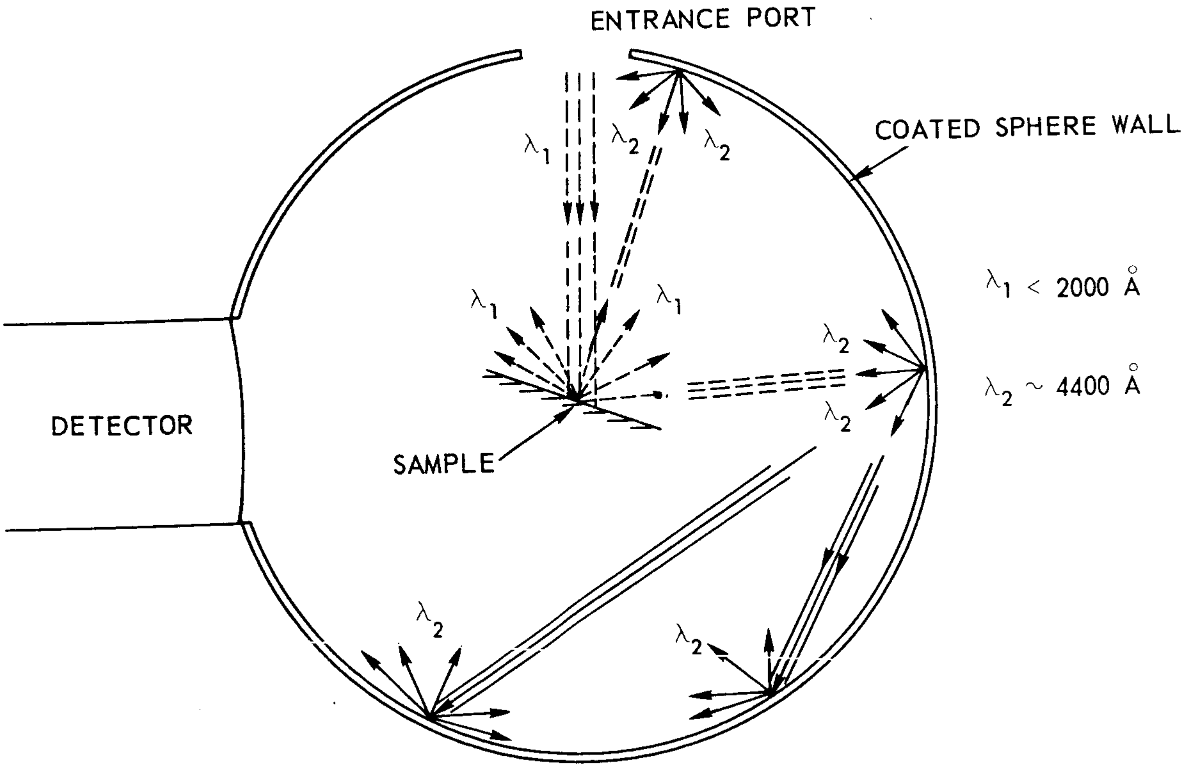


Figure 8b. Typical Situation for a Diffusely Reflecting Sample.

Figure 8

Figure 9

sample drive shaft. The sphere is 4 inches in diameter, with a 1 inch entrance port and a 1.5 inch detector port. Figure 11 shows the sphere and detector housing mounted to the vacuum ultraviolet monochromator, a McPherson model 235 with a Seya-Namioka type of concave grating mount. A capillary discharge type lamp, when used with helium, comprises the ultraviolet light source.

A sketch of the entire single beam system is given in Figure 12a. Figure 12b shows the position of the sample at the geometrical center of the sphere with respect to the incident beam and detector. The sample, a one inch disk, is removed from the beam simply by raising the drive shaft which consists of translational motion through the vacuum seal. The same shaft allows a sample to be rotated with respect to the incident beam, permitting measurements to be made as a function of incidence angle. It also permits a specularly reflecting sample to direct the beam at various points along the sphere wall to test for uniform

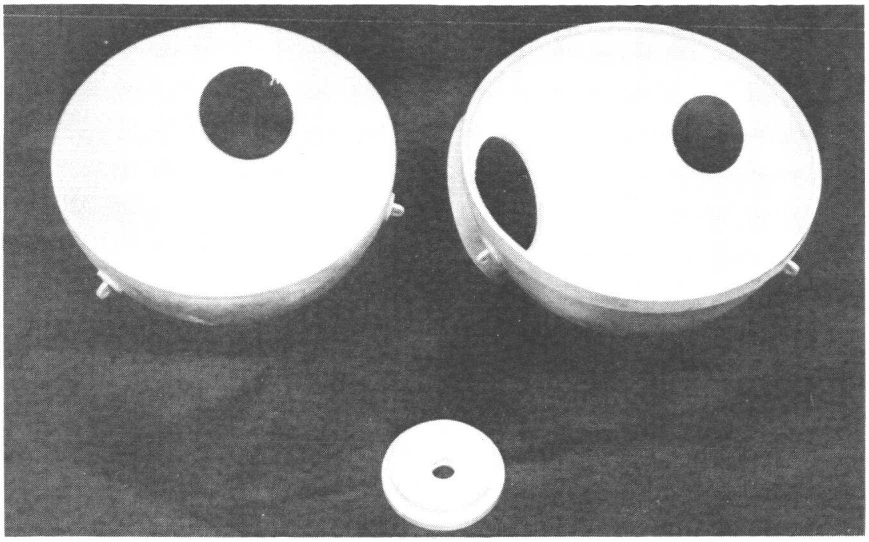


Figure 10

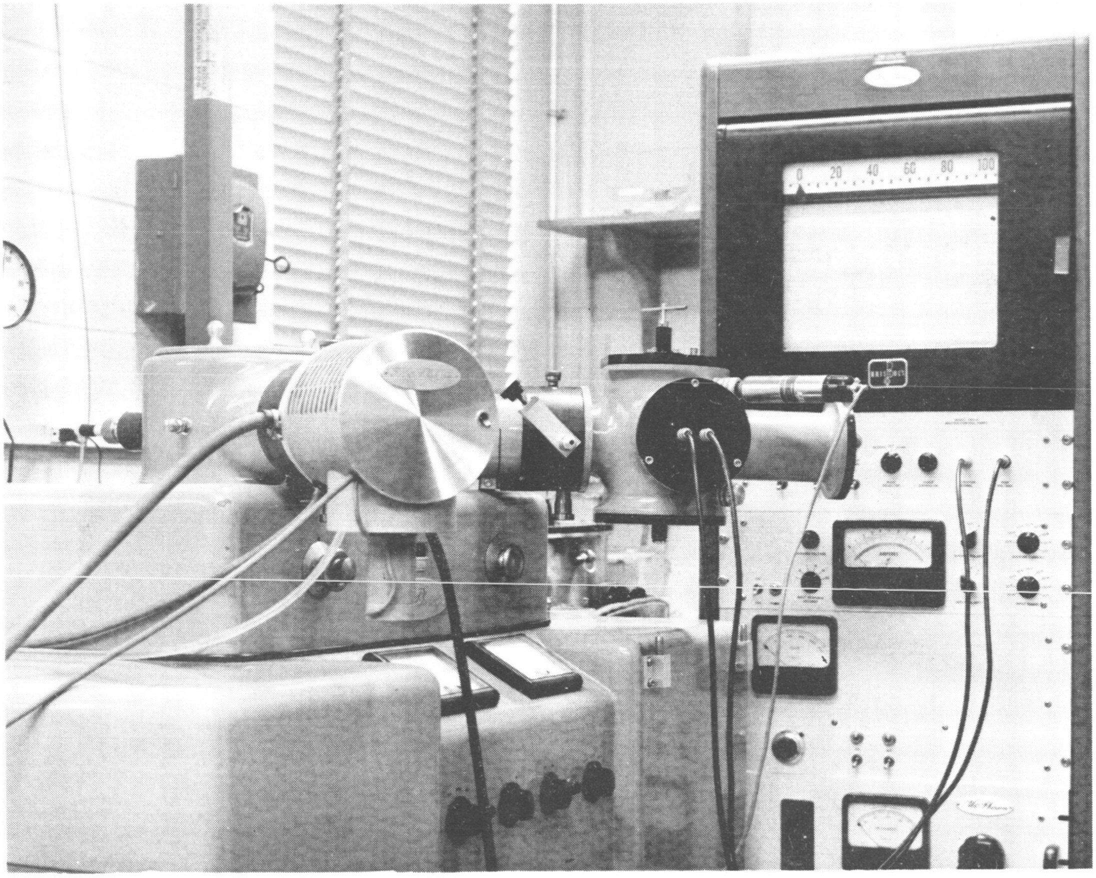
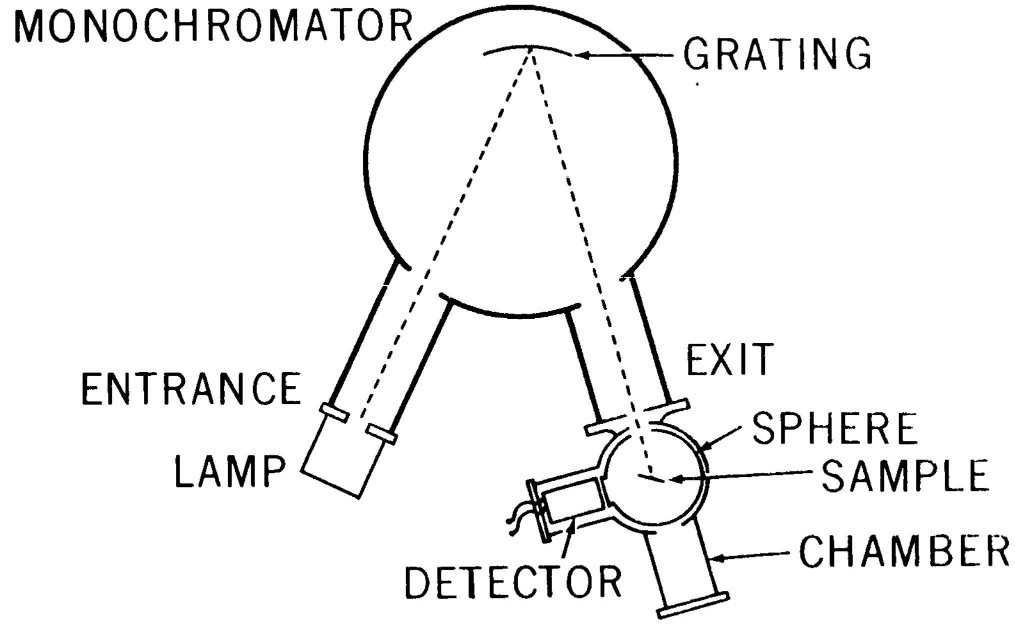
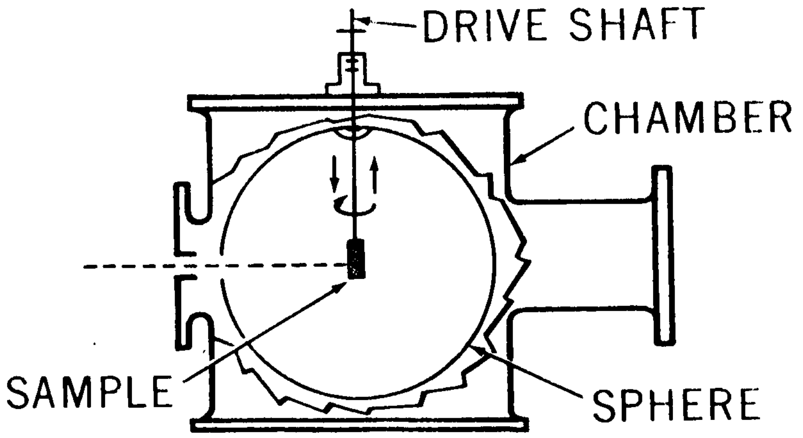


Figure 11

sensitivity of the wall coating, provided the angular reflectance of the sample is known.



A) SCHEMATIC ARRANGEMENT OF SPECTROPHOTOMETER



B) CUTAWAY VIEW OF CHAMBER AND SPHERE

Figure 12. Instrumental Arrangement

The integrating sphere as it is used here is an absolute type of instrument. The incident monochromatic beam strikes the sphere wall and establishes a reference signal in the detector electronics. Then the sample is lowered into the beam which is now diffusely reflected toward the wall, thus establishing a sample signal level. A ratio of the two signals yields the sample's reflectance.

## RESULTS

The results of measurements made on three white pigmented paints — aluminum oxide, titanium dioxide and zinc oxide — are given in Figure 13. The solid blocks and cross lines merely identify the curves and do not correspond to measurement points. Measurements were made on a point to point basis at wavelengths corresponding to strong emission lines in the helium spectrum from 584Å to approximately 2000Å. Because the total area of the sphere ports and sample holder was relatively large, it was necessary to correct the data for losses due to the design limitations of the sphere. However, these corrections amounted to less than two percent of the maximum reference signal level.

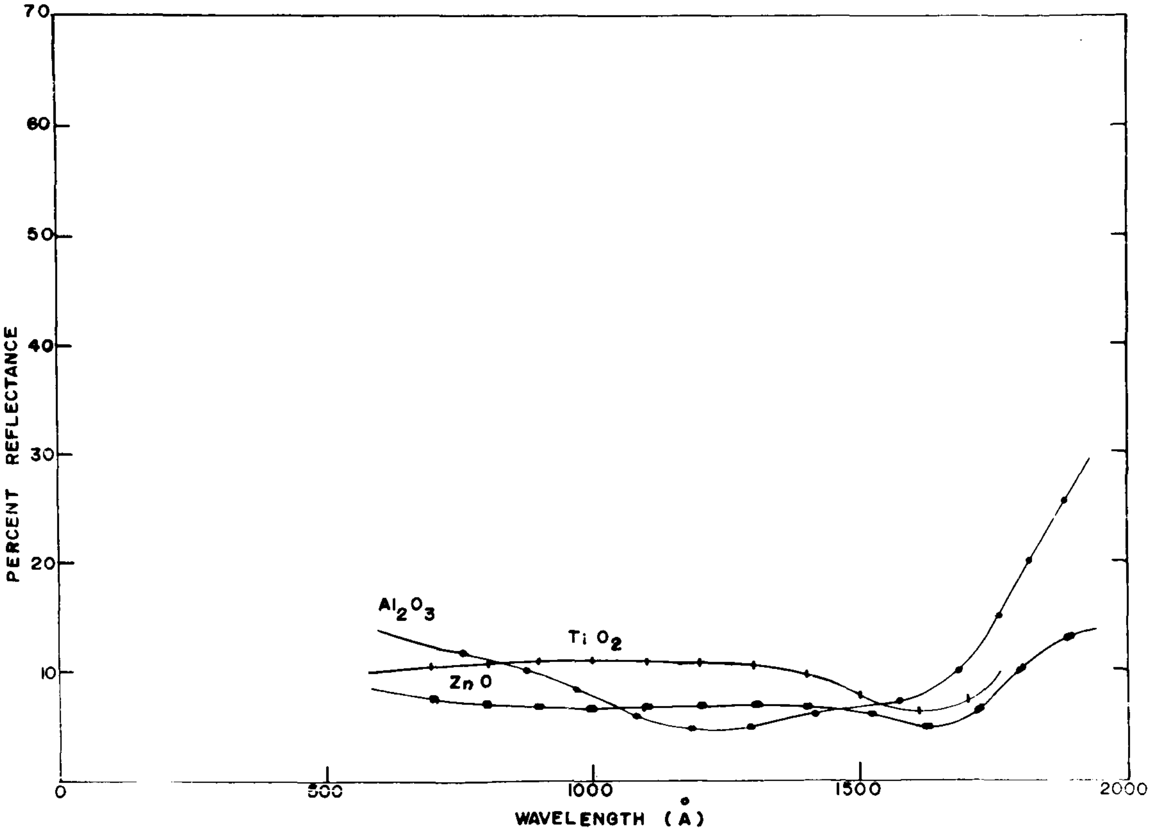


Figure 13

## CONCLUSIONS

The purpose of the work described above is to demonstrate the feasibility of constructing an integrating sphere, of standard design, to be used in the low ultraviolet spectral region. A novel coating was required which would maintain a workable sphere efficiency and it has been shown that sodium salicylate, with proper undercoating, satisfies this requirement. It is doubtful that a sphere whose interior wall had been made diffuse by roughening and then overcoated with evaporated aluminum and magnesium fluoride would maintain an efficiency suitable for operating at low wavelengths. However, this is an alternative worth exploring. The advantage of using a fluorescent coating lies in the fact that the effective reflectance of the sphere wall at low wavelengths can be increased. Its disadvantages arise in the potential non-uniformity of such a coating both in thickness and local sensitivity. These disadvantages have been overcome in the work presented here and it is hoped that an improved sphere will be constructed which will incorporate a design allowing more precise reflectance measurements to be made.

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