PROFESSOR THEODORE LYMAN
(1874–1954)

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VIKTOR SCHUMANN
(1841–1913)

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Techniques of

VACUUM ULTRAVIOLET SPECTROSCOPY

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To Mary, Ross, and Scott

7.2 FLUORESCENT MATERIALS

Soon after the first successful photomultiplier was constructed by Zworykin et al. [10] in 1936, the combination of a photomultiplier with a scintillator was commonly used to detect γ rays and nuclear particles. The technique was soon applied to the detection of ultraviolet radiation. Parkinson and Williams in 1949 were probably the first to sensitize a photomultiplier for the detection of vacuum uv radiation [11]. In their work they used a manganese activated willemite phosphor which responded down to 1450 Å. Johnson, Watanabe, and Tousey [4] in 1951 studied several fluorescent materials in the wavelength range from 850 to 2000 Å. Included in this group of materials was the phosphor sodium salicylate. They found that sodium salicylate had one of the highest fluorescent efficiencies (a response which was constant to within ± 20 per cent over the range 850–2000 Å), was easily prepared, and was not affected by a vacuum. Watanabe and Inn [12] repeated and confirmed the fluorescent yield experiments on sodium salicylate over the same spectral range. They included one point at 584 Å which lay 15 per cent lower than their mean efficiency value. These ideal qualities shown by sodium salicylate have made it the most commonly used sensitizer for the detection of vacuum uv radiation.

Sodium Salicylate

Probably the earliest investigation of the relative fluorescent yield of sodium salicylate was carried out by Déjardin and Schwégler in 1934 [13]. They reported a constant fluorescent efficiency between 2200 and 3400 Å. Since then, others have confirmed the results for wavelengths longer than 2000 Å [14,15]. For wavelengths shorter than 2000 Å, recent results have shown that the fluorescent efficiency is not always constant as a function of wavelength [16–19]. There appears to be an aging effect which reduces the efficiency more at the shorter wavelengths. This aging effect is possibly due to the vacuum environment, which in most vacuum monochromators contains contaminants such as oil vapors. Allison et al. [20] have studied the aging effect at 1216, 1608, and 2537 Å, taking great care to keep the sodium salicylate samples in a very clean vacuum, and have observed no deterioration at these wavelengths. Although some doubts have arisen as to the constancy of its fluorescent efficiency, sodium salicylate still appears to be the most useful phosphor for detection of vacuum ultraviolet radiation. Consequently its properties will be discussed below in detail.

Preparation. Sodium salicylate is obtained as a very fine crystalline powder which can be dissolved in methyl alcohol. After forming a saturated solution, it is sprayed onto a glass slide or directly onto the glass envelope of a photomultiplier using an atomizer or spray gun. A heat gun is used to blow hot air continually onto the window to facilitate the evaporation of the alcohol. This procedure produces a fine crystalline layer of sodium salicylate. The spraying is continued until the glass surface is all covered and the desired thickness is obtained.

Efficiency versus Thickness. There appears to be unanimous agreement among the several investigators who have studied the effect of thickness

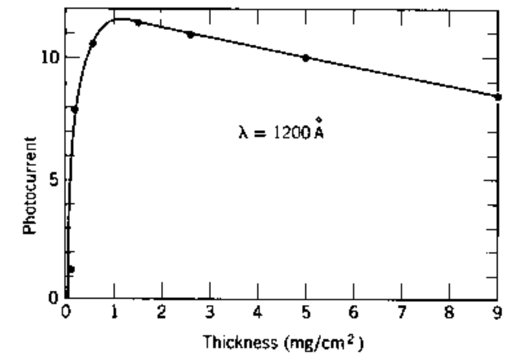

Fig. 7.3 Relation between response and thickness of sodium salicylate layer at 1200 Å (courtesy M. Seya and F. Masuda [21]).

on the fluorescent efficiency that a surface density of approximately 1 mg per cm² will give the optimum response [21–24]. This value appears to be independent of wavelength from 584 to 2200 Å. Figure 7.3 reproduces the work of Seya and Masuda at 1200 Å [21]. It can be seen that the efficiency rises rapidly to a maximum at 1 mg per cm² then falls off very slowly as the thickness increases.

Fluorescent Spectrum and Decay Time. The fluorescent spectrum of sodium salicylate was first measured by Thurnau [25] who also found that the spectrum was independent of the exciting wavelength between 275 and 2537 Å. Hammann [14] has shown this to be true from 2800 to 3600 Å. Figure 7.4 shows the relative intensity of the emission spectrum as a function of wavelength. The maximum intensity of fluorescence is located at 4200 Å and coincides with the maximum sensitivity of a photomultiplier with an S11 cathode.

The fluorescent decay time of sodium salicylate appears to lie between 7 and 12 nsec. Early measurements by Nygaard and Sigmond [26] in 1961

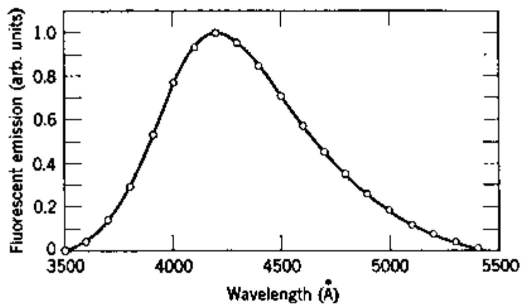

Fig. 7.4 Fluorescent emission spectrum of sodium salicylate (courtesy E. C. Bruner [19]).

gave a value of 12 nsec; however, Nygaard [27] quotes more recent and accurate measurements as having given 7 nsec. Independent measurements by Herb and Sciver [28] give a value between 8.5 and 10 nsec.

Relative Fluorescent Quantum Efficiency. With the exception of the original results reported by Johnson et al. [4] and by Watanabe and Inn [12] regarding the constancy of the relative fluorescent efficiency of sodium salicylate, most subsequent observers have noted a decrease in efficiency for wavelengths between 1600 and 1000 Å [16–19]. The decrease is minimal for a freshly prepared salicylate film which has not been exposed to a typical vacuum monochromator environment for long. Figure 7.5 shows the aging effect for a sample approximately 280 hours old compared to a sample 1 hour old [16]. Where the fresh sample had a constant efficiency

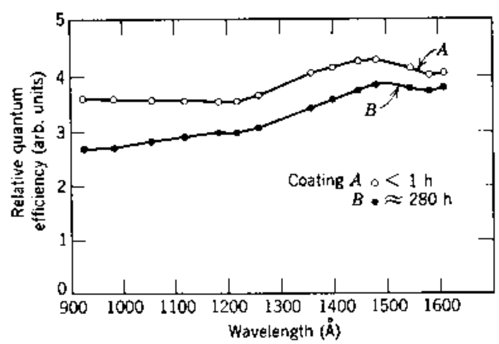

Fig. 7.5 Relative quantum efficiency of sodium salicylate between 900 and 1600 Å. The yield was measured for two different coatings relative to a thermopile. Coating *A* is less than one hour old while coating *B* is approximately 280 hours old (Samson [16]).

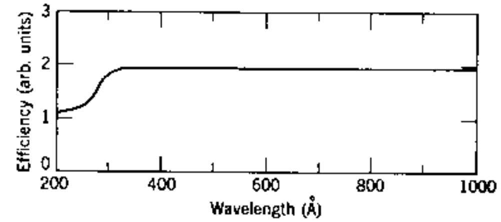

Fig. 7.6 Relative quantum efficiency of sodium salicylate between 200 and 1000 Å.

between 900 and 1216 Å, the 280-hour old sample was 12 per cent lower at 900 than at 1216 Å. Below 1000 Å, the relative efficiency remains constant down to 300 Å, then rapidly decreases by about 50 per cent between 200 and 300 Å. The relative efficiency of sodium salicylate between 200 and 1000 Å is shown in Fig. 7.6 [29]. The efficiency in this case is expressed in terms of the ratio of the photomultiplier output current to the absolute intensity of the incident light (expressed in photons/sec). The absolute intensity being measured with a rare gas ion chamber.

Absolute Fluorescent Quantum Efficiency. As mentioned above, the fluorescent quantum efficiency has been observed to change with age. This fact would seem to make it meaningless to talk about an absolute efficiency. However, even although aging takes place, it probably is possible to determine the intensity of a source to within an order of magnitude using a sodium salicylate coated photomultiplier. Thus it is desirable to determine the absolute efficiency of sodium salicylate as accurately as possible. Table 7.1 lists the various values obtained by different groups. The spread in the results undoubtedly is caused, in part, by samples of different thicknesses and age. However, the spread may also be caused by the different experimental techniques employed. With the exception of Studer [30], all of the investigators have used thin coatings of sodium salicylate on a glass substrate, the sodium salicylate being first dissolved in methyl alcohol. Studer, however, compressed the salicylate to form a plaque about 2 mm thick and then compared the reflected and fluorescent radiation from this plaque with a similar one formed from MgO. He has assumed that all of the fluorescent radiation is emitted from the surface of the salicylate plaque that faces the incident radiation. This assumption is based on the supposition that the sodium salicylate plaque, as that of MgO, has a reflectance approaching 100 per cent. If this assumption is not valid, the absolute efficiency of salicylate will be greater than 60 per cent. However, in a separate experiment, Studer has compared the fluorescence from a sodium salicylate plaque with that from a $MgWO_4$ plaque and has again arrived at an efficiency of approximately 60 per cent, which is about the average value listed in Table 7.1.

Allison et al. [22] have shown that the angular distribution of the fluorescent radiation for films 2-4 mg per cm^2 varies as the cosine of the angle measured from the direction of the incident exciting radiation. Taking this fact into account and the fact that the response of a photomultiplier varies with the angle of incidence of the radiation, Nygaard [31] has shown that his previous determination of 50 per cent for the absolute efficiency was too small, but the magnitude is unknown. The value of

Table 7.1 Absolute Quantum Efficiency of Sodium Salicylate

	Absolute Efficiency			Layer Thickness	
Observer	2537 Å	1216 Å	304 Å	(mg/cm^2)	References
Allison *et al.*	99	94		2–4	[22]
Bruner		62–80	41	5	[19]
Vasseur and Cantin	65	38		2	[18]
Nygaard	50			1 2	[23]
Kristianpoller	64			6	[33]
Inokuchi *et al.*	25			?	[32]
Studer	60			2 mm[a]	[30]

[a] This sample was a pressed plaque 2 mm thick.

25 per cent found by Inokuchi et al. [32] appears to be too low. Thus the main discrepancy at 2537 Å is between the high efficiency found by Allison et al. and the remaining values which lie approximately between 60 and 65 per cent.

From the practical point of view, a value of 65 per cent for the absolute quantum efficiency of sodium salicylate for exciting radiation between 400 and 3400 Å seems to be a suitable compromise. Regardless of any aging effects or of the true quantum efficiency, it is unlikely that the value of 65 per cent will be more than a factor of two in error. It should be noted that Kristianpoller [33] has observed an increase in the fluorescent efficiency of approximately 25 per cent when sodium salicylate is cooled to liquid nitrogen temperature.