



Subject: ARTIFACTS OBSERVED IN SINGLE-BEAM SOURCE
OUTPUT CURVES OF CARY 14'S AND 17'S AND
OTHER GRATING MONOCHROMATOR INSTRUMENTS

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Applications

INTRODUCTION

Scientists who work with spectrophotometers of various kinds are often unaware of the anomalies characteristically associated with grating monochromators. Most UV-visible and IR spectrophotometers are commonly operated in double-beam (DB) mode, and hence, flat baselines are obtained which show no or very minor traces of these anomalies.

When a spectrophotometer is used in the single-beam (SB) mode, however, grating anomalies become quite apparent. One type is commonly called Wood's anomalies, for R. W. Wood who first observed them, although they were theoretically predicted earlier by Lord Rayleigh. They occur at grating angles when orders other than the one used reach grazing angles to the grating surface ($\sin \phi_2 = \text{unity}$, in the grating equation $\sin \phi_1 + \sin \phi_2 = N\lambda/d$ where ϕ_1 and ϕ_2 are angles of incidence and diffraction respectively, N is a positive or negative integer for the order, λ is the wavelength, and d is the spacing of the grating rulings). They are apparently caused by redistribution of the energy of the grazing order among the other orders including the one going out the exit slit. Changes in energy are usually accompanied by changes in polarization.

From this description, it is obvious that any grating monochromator covering a wide wavelength range, e.g. 400-600 nm (hence a wide grating angle), will show Wood's anomalies. No way of avoiding them or compensating their energy and polarization changes has ever been found.

Assuming no sample present, the output curve obtained from a spectrophotometer operated in SB mode is a function of three factors:

- 1) energy distribution of the source,
- 2) transmission and absorption characteristics of the optics including the monochromator, and
- 3) detector response.

This technical memo discusses the transmission characteristics of prism-grating monochromators used in the Cary 14 and 17.

DISCUSSION

If monochromator characteristics were constant, and a SB recording of relative lamp energy versus wavelength was made, then the resultant curve would be a function only of the lamp output and detector response curves. Experimentally this is not found to be the case, as monochromator characteristics contribute significant spectral features to the output. The observed structure can be attributed to:

- 1) Wood's anomalies,
- 2) absorption characteristics of the optical elements in the monochromator and external optics, and
- 3) any unpurged water vapor or CO₂ in the near and fundamental IR regions.

Figure 1 shows an experimental curve typical of that obtained from a Cary 14 or 17 in SB mode using a tungsten lamp and a lead sulfide detector.

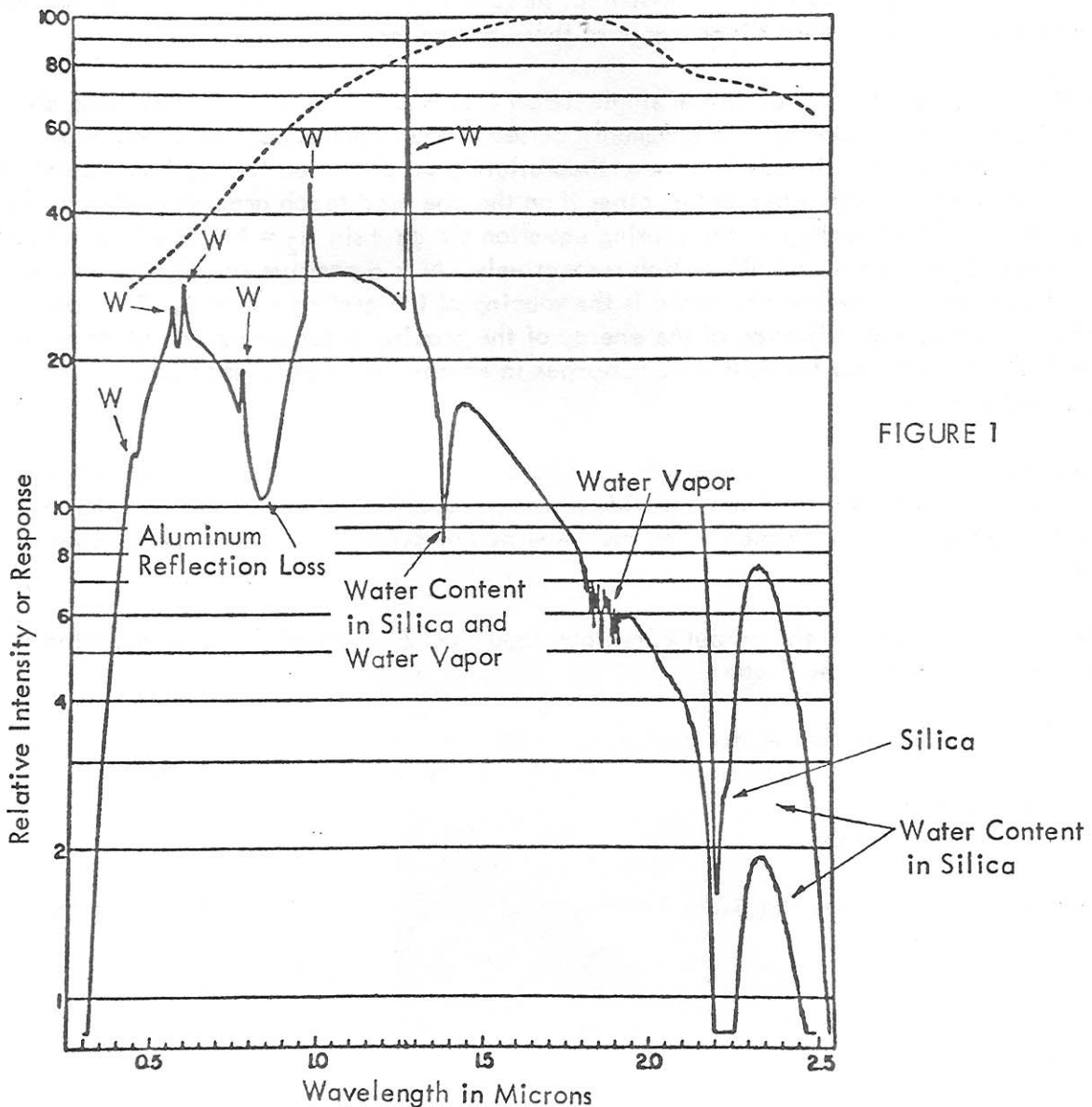


FIGURE 1

(Reproduced from "Artifacts in Emission Spectral Studies By the Cary 14 Spectrophotometer. Corrigendum in the Proposed Singlet Molecular Oxygen Emission from a Tungsten Lamp", A. K. E. Hagopian, J. M. Marrs, and A. U. Khan, *J. Chem. Phys. Lett.* 9: 609 (1971).)

1) Wood's Anomalies--Bands which may be attributed to Wood's anomalies are usually found near the following "Rayleigh" wavelengths:

$$\lambda (\mu) = 0.3175, 0.3464, 0.4085, 0.4232, 0.5437, 0.5725, 0.760, 0.959 \text{ and } 1.259.$$

Such bands in Figure 1 are labeled "W". It should be noted that there will be some variation in peak intensities but not in wavelength, depending on the direction of the beam through the monochromator.

2) Absorption characteristics of optical elements--The curve minimum in Figure 1 at about 0.8 μ is due to absorption by aluminum coatings on various optical elements. The sharp dips at 1.38, 2.2 and 2.5 μ are due to OH absorption by traces of water in the silica prism. The Cary 14 with Infrasil or the Cary 17 with Suprasil W optics minimize the effects of this water absorption.

3) Water Vapor--Fine structure around the 1.38 μ dip and at about 1.8 to 1.9 μ is due to absorption by water vapor. This structure can be eliminated from the spectrum by purging the spectrophotometer with dry air or nitrogen.

CONCLUSION

Most Cary 14 and 17 users operate these instruments in the double-beam mode. Spectra and baselines in this mode are almost entirely unaffected by Wood's anomalies, absorption properties of the optical elements, and atmospheric conditions, unless samples are sensitive to polarization (7). In fact many, if not most, of the Cary users are not even aware of this phenomenon. However, those few users who operate their instruments in the single-beam mode or who use anisotropic crystalline samples should be aware of the features observed in the curve of Figure 1, to avoid the possibility of confusion or misinterpretation of data.

BIBLIOGRAPHY

The following publications discuss in detail Wood's anomalies and polarization characteristics of the Cary 14 and 17 prism-grating double monochromator, and other grating monochromators. In general, customers who desire detailed or theoretical information concerning these subjects should be directed to these papers. Papers 6 and 7 relate most directly to the material discussed in this memo.

1. Fano, U, "The Theory Of Anomalous Diffraction Gratings And Of Quasi-Stationary Waves On Metallic Surfaces (Sommerfeld's Waves)", J. Opt. Soc. Am. 31: 213 (1941).
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8. "Diffraction Grating Handbook, published by Bausch and Lomb, Inc., Rochester, N.Y. 1970, pages 34-36.