

5-17-1983

# Optical spectrometry via photoelectron spectroscopy

Marshall Clemens

Follow this and additional works at: <http://scholarworks.rit.edu/theses>

---

## Recommended Citation

Clemens, Marshall, "Optical spectrometry via photoelectron spectroscopy" (1983). Thesis. Rochester Institute of Technology. Accessed from

This Thesis is brought to you for free and open access by the Thesis/Dissertation Collections at RIT Scholar Works. It has been accepted for inclusion in Theses by an authorized administrator of RIT Scholar Works. For more information, please contact [ritscholarworks@rit.edu](mailto:ritscholarworks@rit.edu).

OPTICAL SPECTROMETRY  
VIA  
PHOTOELECTRON SPECTROSCOPY

by  
Marshall Clemens

A thesis submitted in partial fulfillment  
of the requirements for the degree of  
Bachelor of Science in the School of  
Photographic Arts and Sciences in the  
College of Graphic Arts and Photography  
of the Rochester Institute of Technology

Signature of the Author \_\_\_\_\_ Marshall Clemens  
Photographic Science and  
Instrumentation Division

Certified by \_\_\_\_\_ Unknown  
Thesis Advisor

Accepted by \_\_\_\_\_ Ronald Fraunis  
Coordinator, Undergraduate Research

THESIS RELEASE PERMISSION FORM  
ROCHESTER INSTITUTE OF TECHNOLOGY  
COLLEGE OF GRAPHIC ARTS AND PHOTOGRAPHY

Title of Thesis: Optical Spectrometry via Photoelectron Spectroscopy

I, Marshall Clemens, hereby grant permission to the Wallace Memorial Library of R.I.T. to reproduce my thesis in whole or in part. Any reproduction will not be for commercial use or profit.

Date: 5/17/83

OPTICAL SPECTROMETRY  
VIA  
PHOTOELECTRON SPECTROSCOPY

by

Marshall Clemens

Submitted to the  
Photographic Science and Instrumentation Division  
in partial fulfillment of the requirements  
for the Bachelor of Science degree  
at the Rochester Institute of Technology

ABSTRACT

The feasibility of performing optical spectrometry via photoelectron spectroscopy was investigated. The energy distribution of photoelectrons should yield information about the spectral distribution of the incident photons, due to the relationship between photon and photoelectron energy. The photoelectron energy distribution from a semi-transparent Sb layer under Hg-arc illumination was measured, using a spherical-geometry ac photoelectron spectrometer. Attempts to produce a CsSb photocathode, which would both increase the quantum yield over a "pure" Sb photocathode and decrease the work function into the visible range, were unsuccessful. This limitation prevented the collection of data relevant to the viability of photoelectron spectroscopy as a measure of incident photon spectral distribution.

## ACKNOWLEDGEMENTS

The author would like to express special thanks to Dr. Merle N. Hirsh, who generously donated time and equipment to the success of this thesis. It certainly would have been impossible without his valuable and good-natured assistance.

Acknowledgement and appreciation is also given to Fuji Photo Film U.S.A. Inc. for their generous scholarship.

## TABLE OF CONTENTS

	Page
Introduction	1
Experimental	4
Results	11
Discussion	14
Conclusions	16
References	17
Vita	18

## TABLE OF FIGURES

	Page
Fig. 1. Spherical-geometry phototube in operation.	5
Fig. 2. a) Example of Photocurrent ( $I_p$ ) vs. Retarding Potential ( $V_R$ ) measurement. b) The derivative of the $I_p$ vs. $V_R$ curve ( $-dI_p/dV_R$ ) is the desired EDC.	5
Fig. 3. Block diagram of the photoelectron spectrometer electronics system.	6
Fig. 4. Retarding Potential and Capacitive balance circuitry.	6
Fig. 5. Vacuum/spectrometer apparatus showing configuration for evaporating Cr and Sb, and glass side-arm for releasing Cs.	8
Fig. 6. Photocurrent ( $I_p$ ) vs. Retarding Potential ( $V_R$ ) for Sb under Hg-arc illumination.	12
Fig. 7. Photoelectron Energy Distribution Curve (EDC) for Sb under Hg-arc illumination.	12
Fig. 8. Comparison of EDC by graphical differentiation vs. ac differentiating technique.	12

## INTRODUCTION

The photoelectric effect has long been a phenomenon of great scientific and practical interest. Its application to photomultiplier and image pickup tubes has yielded a wealth of instruments. Most recently the field of photoelectron spectroscopy has developed as a tool for chemical analysis.

In photoelectron spectroscopy, incident radiation causes the emission of photoelectrons from the material under study. The energy and angular distribution of these photoelectrons provides information about the electron orbital structure of the material. In photomultiplier and image pickup tubes, radiation is detected via photoelectrons that are electrostatically accelerated, then collected, thus ignoring the photoelectron energy distribution. The energy of these electrons follows the familiar equation:

$$\text{Eq. 1: } E (\text{photoelectron max.}) = h\nu - w$$

where  $w$  is the work function of the material. Thus the maximum photoelectron energy is simply related to the incident photon energy. Therefore, it should be possible to determine the spectral distribution of a radiation source by analyzing the photoelectron energy distribution curve (EDC) produced by that source.

There are, however, three important processes that cause the emission of photoelectrons with energy less than that predicted by



equation 1. First, the photoelectrons may undergo inelastic scattering before emerging from the material. In semiconductor photocathodes, such as CsSb, the onset of serious inelastic scattering begins only as the photoelectron energy becomes great enough to undergo scattering by valence electrons. For CsSb this energy is about 4 eV, corresponding to a wavelength of 310 nm. For photon energies greater than 4 eV, scattering begins to destroy the photon-photoelectron energy relationship.<sup>1</sup>

Second, photoelectrons produced by monochromatic radiation will emerge with a range of energies corresponding to the valence-band energy width, i.e., the valence band density of states (VB DOS). An image of the VB DOS is in fact observed in EDC's produced from monochromatic radiation.<sup>2</sup> This phenomenon can severely degrade the impulse response of the proposed photoelectron-optical spectrometer as the VB DOS may be 2 eV wide.<sup>3</sup>

Finally, the energy of the photon may not be conserved due to a non-direct transition. In a non-direct transition the transition probability is such that the photoelectron emerges at an energy lower than that predicted by  $E = h\nu - \phi$ , the extra energy possibly going into lattice vibrations.<sup>4</sup>

The optical spectrometer proposed would consist of a semi-transparent photocathode, for example CsSb, centered in a spherical-geometry ac photoelectron spectrometer. The processes mentioned above would give rise to significant photon to photoelectron energy spread functions. The system impulse response (from a monochromatic input) would be measured at a series of wavelengths. For any non-

monochromatic or continuous source, the EDC would be a linear combination of the corresponding impulse responses. A computer data-analysis program would be used to convert the EDC back to the desired photon energy distribution.

## EXPERIMENTAL

The spherical-geometry ac photoelectron spectrometer was fashioned after that reported by Berglund and Spicer<sup>5</sup> and as improved by R.C. Eden.<sup>6</sup> Fig. 1 shows the spherical phototube in operation. A retarding potential,  $V_R$ , is applied between the photocathode and the spherical, electron-collecting, anode. Photoelectrons with energy less than  $eV_R$  are deflected and return to the photocathode. Electrons whose energy is greater than  $eV_R$  travel to the collecting sphere anode and the resulting photocurrent is measured by the external circuitry.

Fig. 2 illustrates a possible photocurrent vs. retarding potential curve. All photoelectrons with energy less than  $eV_R$  are eliminated from the photocurrent,  $I_p$ , as  $V_R$  is increased. It is apparent that the derivative of this curve,  $dI_p/dV_R$ , plotted vs.  $V_R$  is the desired photoelectron energy distribution curve (or EDC) as shown in Fig. 2.b.

To derive  $dI_p/dV_R$ , a small ac potential,  $V_{ac}$ , is superimposed on  $V_R$  (Fig. 2.a). By measuring  $I_{ac}/V_{ac}$  with a lock in amplifier, the value of  $dI_p/dV_R$  is directly obtained.

A block-diagram of the complete system and schematic of the capacitive balance and retarding potential circuitry is shown in Figs. 3, and 4. The dc retarding potential,  $V_R$ , is slowly scanned from 0-2.0 V by turning a ten turn potentiometer ( $R_1$ ) with a small synchronous moter. The ac voltage is fed to the phototube via the transformer  $T_1$ , and to the lock-in amplifier as a reference signal. The variable capaci-

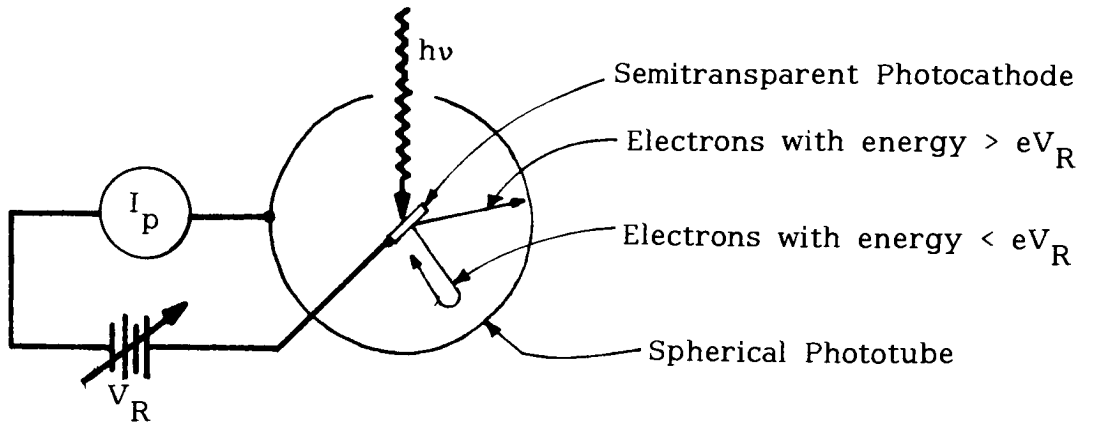


Fig. 1. Spherical-geometry phototube in operation.

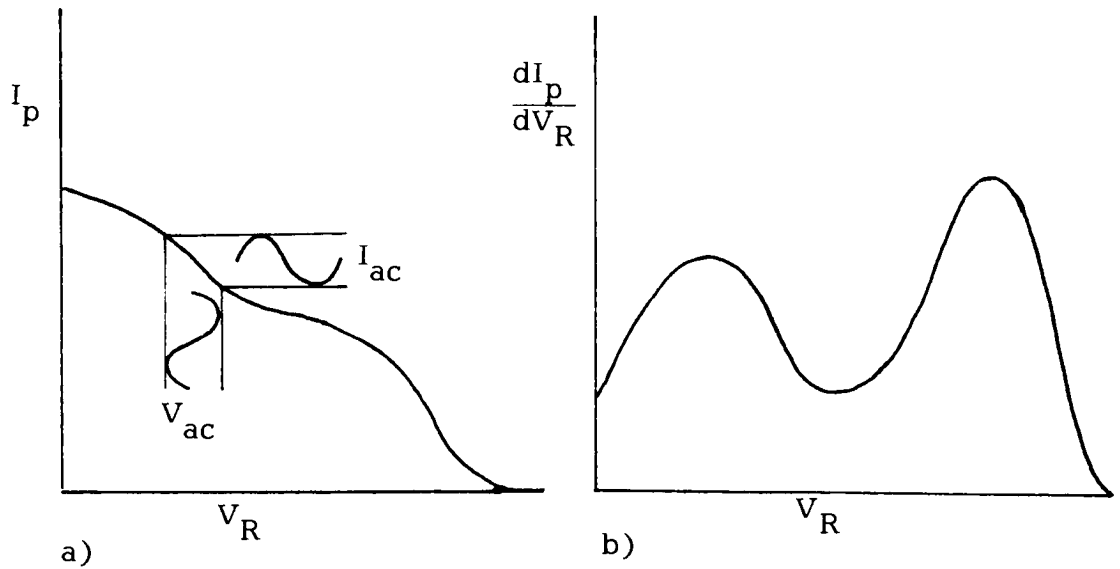


Fig. 2. a) Example of Photocurrent ( $I_p$ ) vs. Retarding Potential ( $V_R$ ) measurement. b) The derivative of the  $I_p$  vs.  $V_R$  curve ( $-dI_p/dV_R$ ) is the desired EDC.

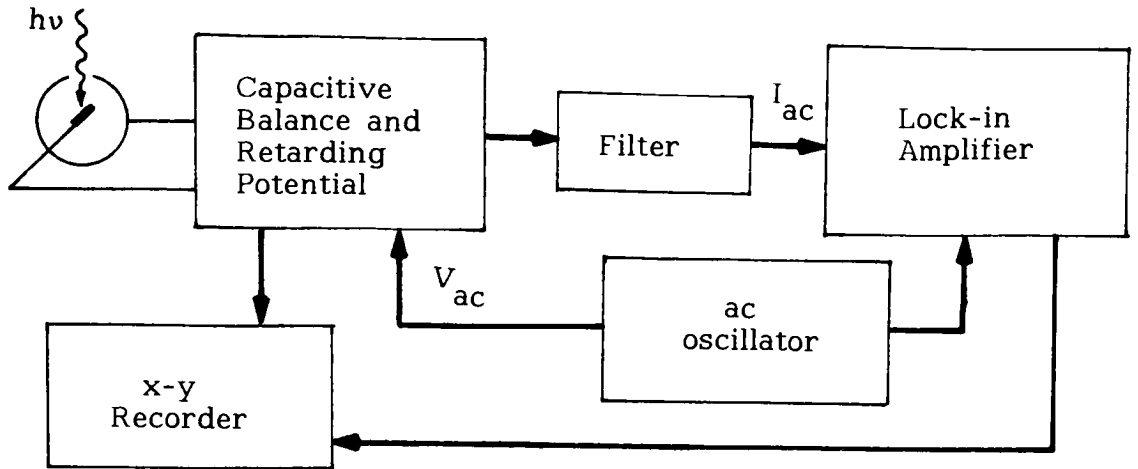


Fig. 3. Block diagram of the photoelectron spectrometer electronics system.

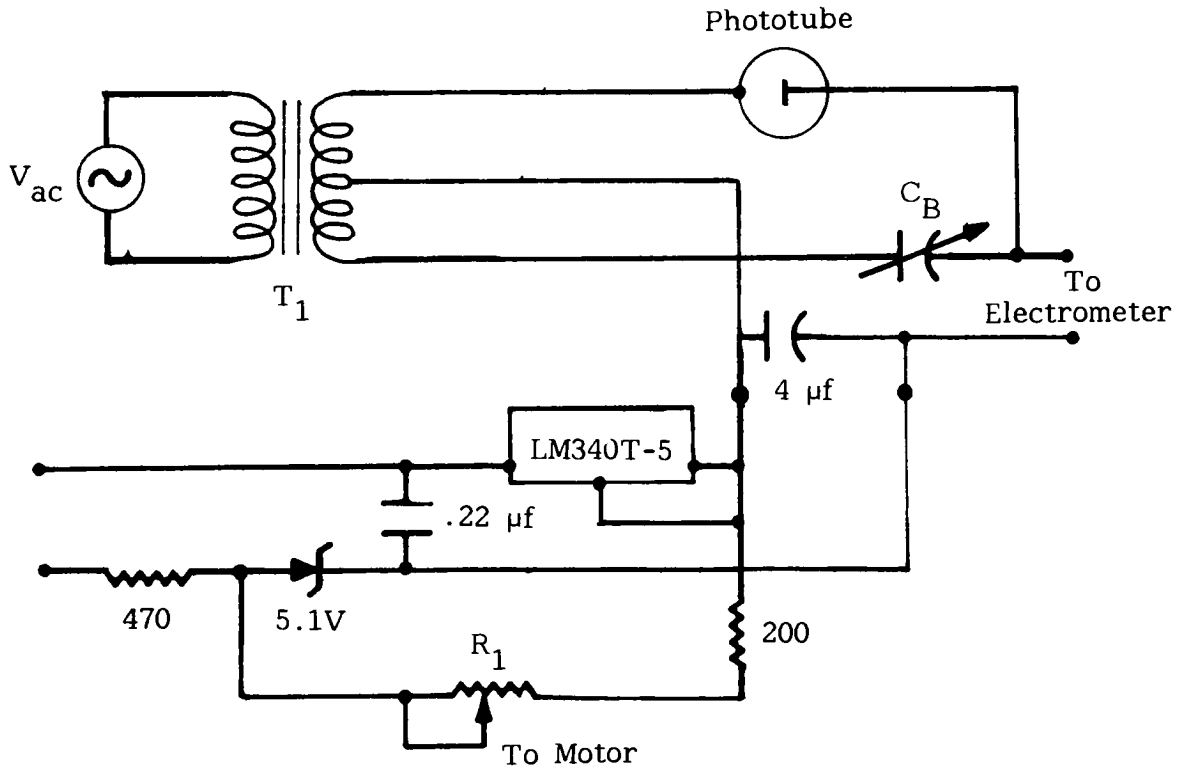


Fig. 4. Retarding Potential and Capacitive balance circuitry.

tor,  $C_B$ , is necessary to balance the ac capacitive current that would result from applying an ac voltage to the phototube alone. The electrometer amplifies the ac and dc photocurrents, the dc being rejected by the filter before entering the lock-in amplifier. For a constant  $V_{ac}$  (from the ac oscillator),  $i_{ac}$  (from the phototube) is measured by the lock-in amplifier and fed to the recorder y-axis;  $V_R$  is fed to the recorder x-axis. Photocurrent vs.  $V_R$  curves can be recorded by simply connecting the electrometer directly to the recorder y-axis (and setting  $V_{ac}=0$ ).

Since the photocathode sensitivity is destroyed by exposure to air, it must be fabricated while centered in the phototube and under vacuum. The fabrication of the semitransparent CsSb photocathode begins with the vacuum deposition of a thin conductive layer ( $ND = .1$ ) of a material such as chromium onto the glass or quartz substrate. This layer is needed to replenish the electrons lost by photoemission, as the thin CsSb layer has high resistance. Next, a thin layer of Sb is vacuum evaporated on top of the chromium. This Sb layer is then reacted with Cs vapor at a temperature of  $150^\circ\text{C}$  to form the  $\text{CsSb}_3$  photoemissive compound.<sup>7</sup>

The preferred method for releasing Cs vapor is by reaction of  $\text{CsCr}_4$  with a suitable reducing agent.<sup>8</sup> Unfortunately a supply of  $\text{CsCr}_4$  was unavailable. It was then decided to release Cs vapor from an ampule of Cs metal via glass side arm.

Fig. 5 shows the vacuum-spectrometer apparatus employed. The phototube is a 4" dia. copper sphere, separable into hemispheres to allow access to the photocathode. A 1" dia. hole in the top of the

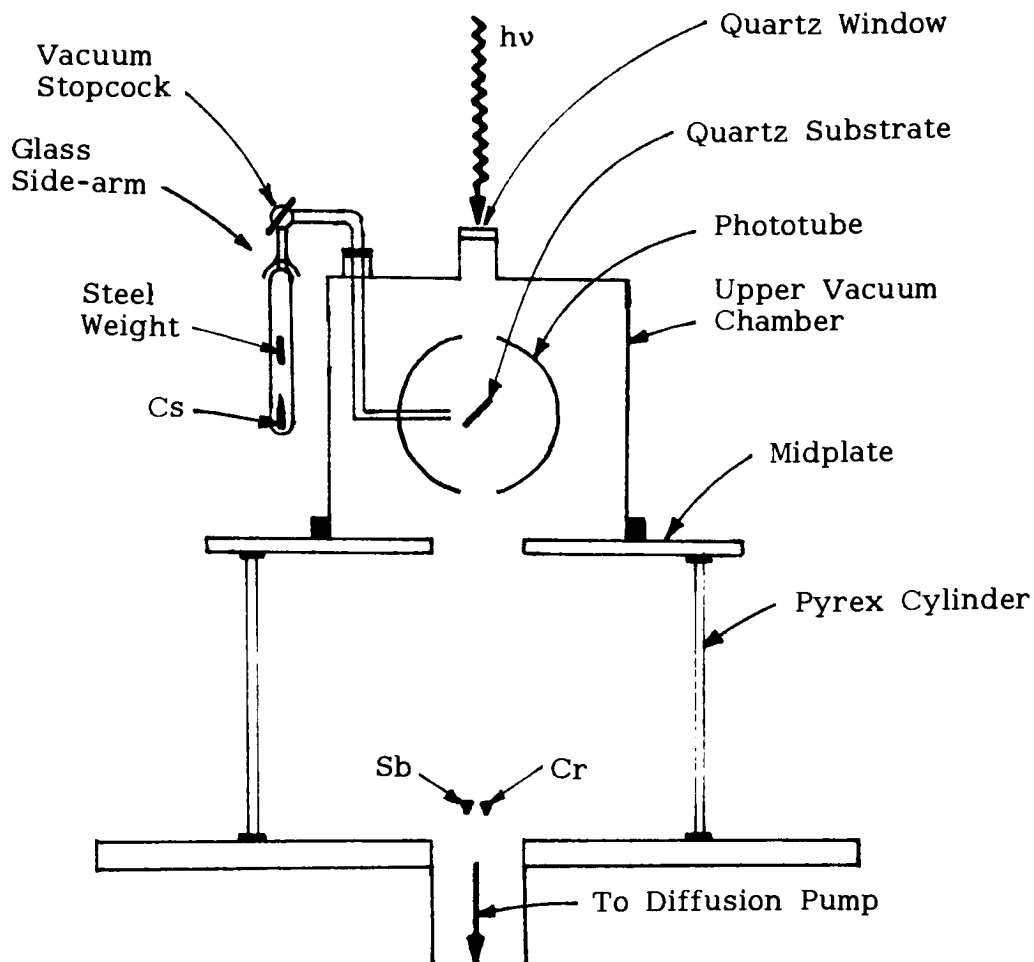


Fig. 5. Vacuum/spectrometer apparatus showing configuration for evaporating Cr and Sb, and glass side-arm for releasing Cs.

sphere allows radiation to enter and strike the photocathode. A 1" hole in the bottom allows the evaporation of Cr and Sb onto the quartz substrate. The quartz substrate is held by a loop of resistive heating wire that raises the quartz temperature to 150°C. Since photoelectron emission intensity follows a cosine distribution around a line perpendicular to the incoming radiation beam, the substrate is positioned at a 42° angle with respect to the vertical incoming beam. Thus the majority of the photoelectrons should be collected in the right center of the sphere, where the electric field should be the most uniform and parallel to the emitted photoelectrons.

The Cr is vacuum evaporated from a tungsten wire located below the substrate. Sb is evaporated from a carbon boat, also heated by tungsten wire and located below the substrate. The coating thickness is controlled by measuring the transmission of light from an incandescent bulb through the coatings with a light meter positioned outside the quartz window.

The Cs ampule is enclosed in the glass side arm outside the vacuum chamber. When the side-arm is brought under vacuum, a glass-encased steel weight is dropped on the ampule to open it. A vacuum stop-cock controls the Cs flow and seals the broken Cs ampule in vacuum for future use.

Since a vacuum pressure of only roughly  $1 \times 10^{-5}$  Torr was attainable, the vaporization temperature of the Cs was approximately 100°C. Bringing the entire glass side-arm and stop-cock to a temperature of 100°C proved to be impossible, because of the grease on the stopcock. The Cs vapor would then condense on any relatively cold parts of the



tubing. Thus the Cs vapor could not be diffused into the system to react with the Sb layer. This thwarted the attempt to fabricate the CsSb photocathode.

However, the deposition of the Cr and Sb was accomplished, and photoemission from the Sb was obtained using U.V. radiation from a Hg-arc lamp. The photoelectron spectrometer electronics were connected, and the photoelectron energy distribution was obtained.

## RESULTS

The photocurrent vs. retarding potential curves are shown in Fig. 6 with  $\pm 3$  V limits. Due to the low quantum yield of uncesiated metals, the maximum photocurrent ( $V_R = 0$ ) was approximately  $6 \times 10^9$  A. There existed in the circuitry a small dc leakage current, of unknown origin, that caused the electrometer reading to drop as  $V_R$  increased even when no photocurrent was present. This variable dc bias was removed before plotting, but is suspected to contribute to the high variability.

Fig. 7 shows the EDC, with  $\pm 3$  V limits, obtained using the ac differentiation technique. The curve is the average of 12 separate curves obtained over 5 days. Changes in the EDC from day to day are responsible for the high variability. Consecutive runs made on the same day showed good repeatability and low noise.

A comparison of the EDC obtained via the ac technique (Fig. 7) with that obtained by graphical differentiation of the  $I_p$  vs.  $V_R$  curve (Fig. 6) is shown in Fig. 8. With the exception of discrepancies near zero retarding potential, the data are in good agreement. This indicates that the ac photoelectron spectrometer worked quite well.

Since a UV monochromator or appropriate narrow band UV filters were unavailable, it was impossible to test the system response to a monochromatic input. Even if such equipment was available, the extremely small photocurrents resulting from such a narrow-band input

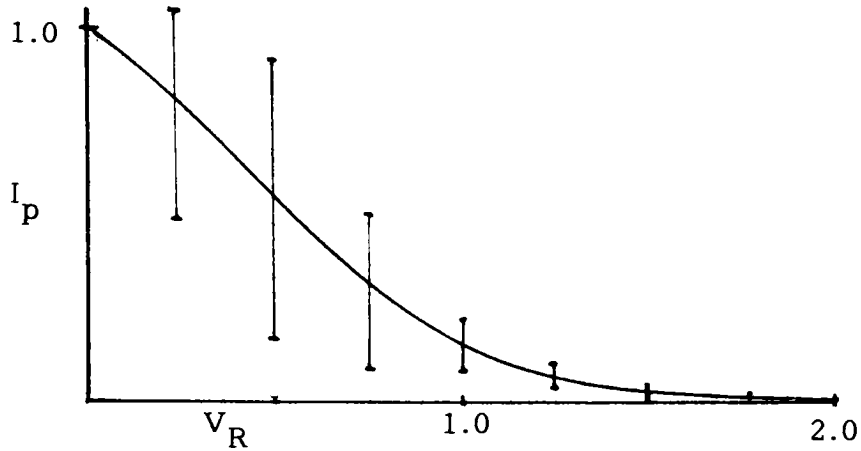


Fig. 6. Photocurrent ( $I_p$ ) vs. Retarding Potential ( $V_R$ ) for Sb under Hg-arc illumination.

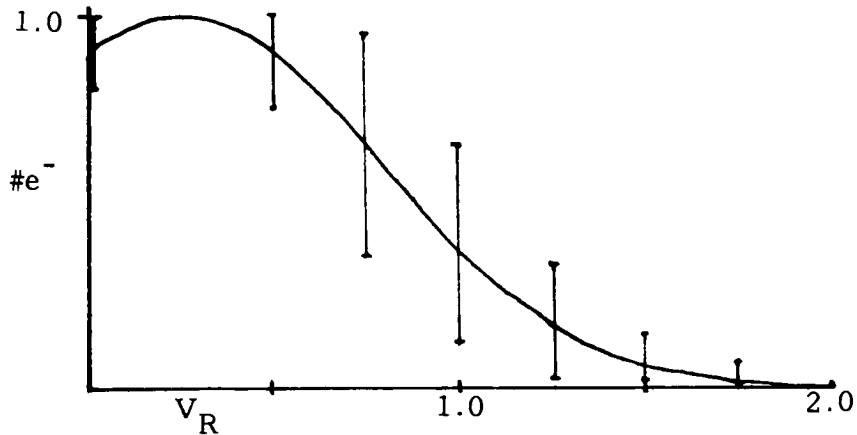


Fig. 7. Photoelectron Energy Distribution Curve (EDC) for Sb under Hg-arc illumination.

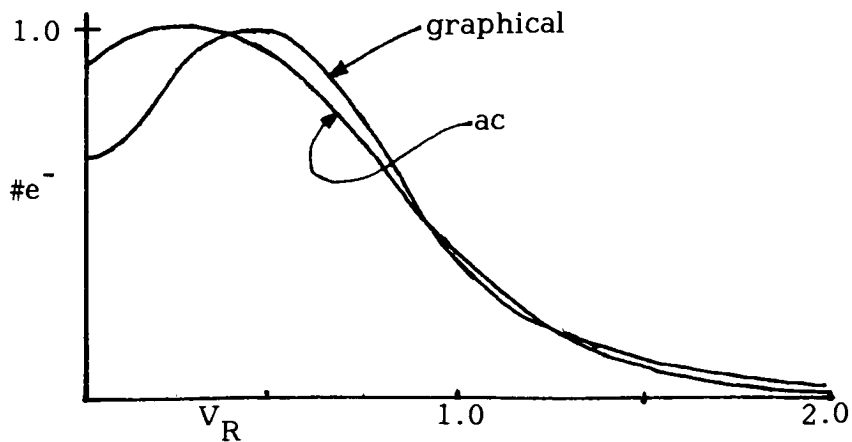


Fig. 8. Comparison of EDC by graphical differentiation vs. ac differentiating technique.

would not have been detectable by the electronic system. Thus no data applicable to the evaluation of optical spectroscopy via photoelectron spectroscopy was obtained.

## DISCUSSION

Although the comparison in Fig. 9 indicates that the photoelectron spectrometer worked well, the energy resolution of the system and electron energy spread function of Sb are unknown. They were not obtained since it was impossible to apply, or measure, the response from a monochromatic UV input.

It is also impossible to predict theoretically what the EDC resulting from Hg-arc illumination should look like. The photoelectric work function of Sb has been reported as both 4.01 and 4.6 eV.<sup>9</sup> Below 250 nm, the amount of radiation emitted from the lamp and passed by the quartz window, quartz substrate, and Cr layer is unknown. Thus the spectral distribution of radiation reaching the Sb layer is unknown.

However, calculating the energy of photoelectrons emitted by 254 nm Hg-line, for a Sb work function of 4.6 eV:

$$E_{\max} = \frac{1.242 \times 10^{-6}}{253 \times 10^{-9}} = 0.29 \text{ eV}$$

An expected photoelectron energy of 0.29 eV is obtained; this should probably be compared with the 0.25 eV peak in the measured EDC.

The work done by Apker, Taft and Dickey<sup>10</sup> on photoemission from CsSb shows that, above 300 nm, the photoelectrons are fairly evenly distributed from an energy predicted by Eq. 1 down to zero. If this is the case for semitransparent CsSb photocathodes, the linear combination

of such responses from a continuous source, would be very difficult to convert back to a photon energy distribution. Thus the spectral resolution of such a device would be severely limited. However, at high photon energies (x-rays, etc.) and looking over a wide wavelength region, this technique might still be a valuable tool. The difficulty in performing spectroscopy at these high photon energies, along with acceptable photoelectron energy spread functions from metals, might produce acceptable wavelength resolution.

## CONCLUSIONS

The construction and operation of a spherical geometry ac photoelectron spectrometer was accomplished, and the photoelectron energy distribution from a semitransparent Sb film under Hg-arc illumination, was recorded. Due to difficulties in producing the Cs vapor necessary to form a CsSb photocathode, data applicable to the evaluation of optical spectroscopy via photoelectron spectroscopy was not collected.

REFERENCES

1. L. Apker, E. Taft, and J. Dickey, J.Q.S.A., 43, 78 (1953).
2. R.A. Powel, W.E. Spicer, G.B. Fisher, and P. Gregory, Phys. Rev. B, 8, 3987 (1973).
3. Ibid.
4. C.N. Berglund and W.E. Spicer, Phys. Rev., 136, A1030 (1965).
5. W.E. Spicer and C.N. Berglund, Rev. Sci. Inst., 35, 1665, (1964).
6. R.C. Eden, Rev. Sci. Inst., 41, 252, (1970).
7. A.H. Sommer, Photoemissive Materials, Robert E. Krieger Publishing Co., Huntington, N.Y., 1980.
8. Ibid.
9. American Institute of Physics Handbook, McGraw Hill, New York, N.Y., 1957.
10. L. Apker, E. Taft, and J. Dickey, J.Q.S.A., 43, 78 (1953).



## VITA

Marshall Clemens was born and raised in Northfield, Illinois, a suburb north of Chicago. His father, a self-employed design engineer, encouraged the development of Marshall's technical background. He attended New Trier West High School before attending RIT in the fall of 1979. Between his sophomore and junior year he spent six months working in the Photographic Technology Department at NASA's Ames Research Center in Mountain View, California. Marshall was a recipient of the 1982-83 Fuji Scholarship.