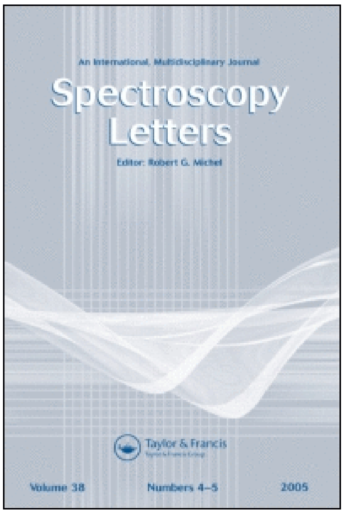

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Preliminary Evaluation of Capabilities of Photoelectric Detection of High Resolution Molecular X-ray Fluorescence Spectra with a 5 M Grating Ultrasoft X-ray Spectrometer

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PRELIMINARY EVALUATION OF CAPABILITIES OF PHOTOELECTRIC DETECTION OF HIGH RESOLUTION MOLECULAR X-RAY FLUORESCENCE SPECTRA WITH A 5 M GRATING ULTRASOFT X-RAY SPECTROMETER

KEY WORDS: X-ray spectroscopy, grating instrumentation, photoelectric detection, molecular electronic structure

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INTRODUCTION

Using our recently developed high resolution 5 M grating spectrograph we have reported previously on the capabilities of photographic detection for obtaining molecular x-ray fluorescence spectra.(1,2) Accordingly, we indicated that in spite of a relatively inexpensive monochromator source the signal to noise ratio on O K in Li_3PO_4 at equivalent instrumental resolution was of the same order of magnitude as that obtained by Wiech's group using photoelectric detection and the DORIS storage ring as a source.(3)

Below we wish to report on our recently developed photoelectric detection capabilities for obtaining high resolution molecular x-ray fluorescence spectra. For the sake of completeness we also provide a comparison of our photographic and photoelectric capabilities.

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DESCRIPTION OF INSTRUMENTATION

The overall instrumentation consists of a 5 M grating spectrometer and a Henke-style source of illumination. One of the unique features of the instrumentation is the availability of variable grazing incidence and the pivoting of the entire spectrograph about the primary slit in order to maintain the viewing of the same spot on the sample at all angles of incidence. Since additional details may be found elsewhere(2), we merely discuss the modification of the instrument for scanning photoelectric detection. In Figure 1 we show the main features of the photoelectric attachment minus the primary slit and grating modules.

The key component of the photoelectric attachment is the massive secondary slit and detector carriage. This carriage has three bridge positions. With the secondary slit mounted on the front bridge (i.e. closest to the grating) it is possible to get as low as 8 A in first order using a laminar 632 l/mm grating. Using the rear bridge the maximum wavelength is about 150 A with a 300 l/mm blazed grating.

The detector carriage driven by the leadscrew nut assembly rides on the Rowland circle reference railing very precisely, namely to ±1 μ.(4) The leadscrew rotation is monitored by a high precision, absolute shaft emoder. The leadscrew is driven from the outside of the chamber by a stepping motor via a gear train to provide steps as small as 1.8 μ on the Rowland circle.

A conventionally styled flow proportional counter (FPC) sealed with thin Formvar films prepared according to Henke's prescription(5) has been used as a detector with propane as the

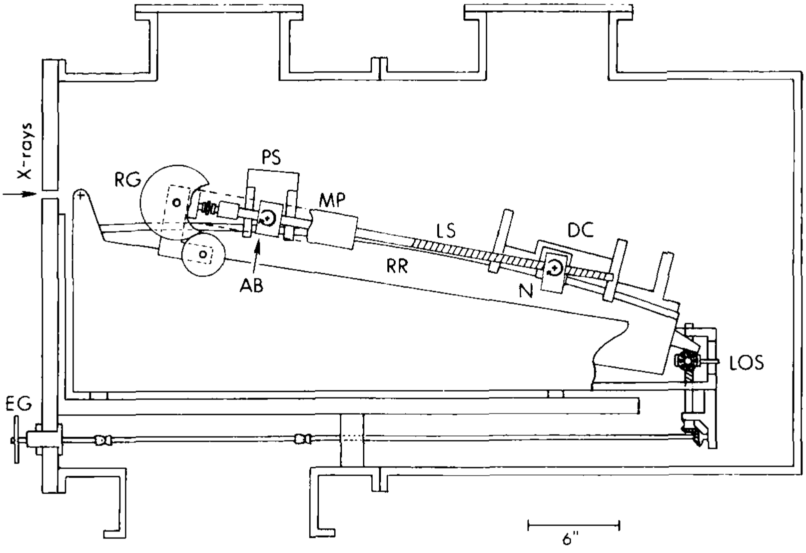

FIG. 1. PHOTOELECTRIC ATTACHMENT FOR THE 5 M GRATING SPECTROMETER. LEGEND: EG -- EXTERNAL GEARS, RG -- REDUCTION GEARS, PS -- PIVOT STAND, AB -- ANCHOR BLOCK, MP -- MOUNTING PLATE, RR -- ROWLAND CIRCLE REFERENCE RAIL, LS -- LEAD SCREW, N -- NUT, DC -- DETECTOR CARRIAGE, LOS -- LINE OF SIGHT ADJUSTMENT.

flow gas at about 75 Torrs of pressure. An HP-85 computer controls, via a microprocessor, the step scan motor and receives shaft encoder and FPC photon output data.

PRELIMINARY EVALUATION

In Figure 2 we depict the essential features of the O K emission spectrum from Li_3PO_4 using our photoelectric scanner at 0.5 eV instrumental resolution. The data were obtained with the 632 l/mm grating at 2° angle of incidence under the following conditions: Primary slit width = secondary slit width = $5\ \mu$, effective secondary slit height = 15 mm, the number of data

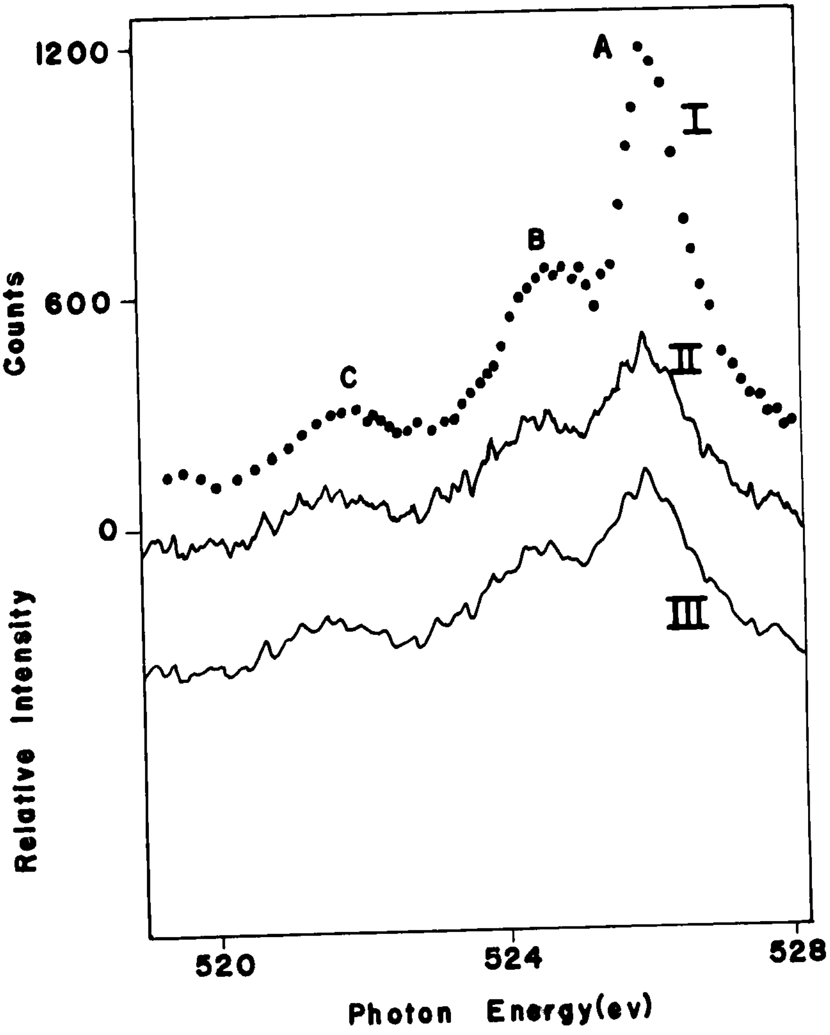

FIG. 2. O K EMISSION SPECTRA FROM Li_3PO_4 WITH 0.5 cV RESOLUTION
I -- PHOTOELECTRIC DATA, II -- RAW PHOTOGRAPHIC DIGITAL DATA,
III -- SMOOTHED PHOTOGRAPHIC DIGITAL DATA (SEE TEXT FOR DETAILS)

points = 70; the interval for each step = 25 μ (about 0.1 eV). While the specific photoelectric data depicted in Figure 2 corresponds to about 1200 counts at peak A achieved in 5 minutes using a Cu anode at a power setting of 9.5 KV and 260 ma, it is possible to get an improvement of a factor of two in count rate by using ultra-thin source and detector windows and obtaining a fortuitously advantageous position of the x-ray tube filament. It should be noted that our count rates are roughly of the same order of magnitude as those reported by Wiech's group, using the DORIS storage ring as a source, but one order of magnitude lower than those reported by Gilberg(6) using a 20 KW rotating anode and 5 cm spectral slit heights.

While a comparison of our photoelectric data with those of Wiech and Gilberg provides a check on the performance of the overall instrumentation approach towards getting high resolution molecular x-ray fluorescence spectra, it is also of considerable interest to ascertain whether or not photographic or scanning photoelectric detection should be used for obtaining such spectra. In this connection it should be noted that the Uppsala group has relied primarily on photographic detection for gathering high resolution spectra from gaseous samples excited by electron bombardment.(7)

A graphical illustration of the comparison between our photographic and photoelectric detection capability is offered in Figure 2 also. We indicate two scans of the O K spectra as obtained by our Bowler Chivens microphotometer in a digitized mode. The first photographic spectrum (II), immediately below the photoelectric scan (I), represents the raw data taken at every 5 μ. The second spectrum III corresponds to averaging over five points. The spectrographic slit resolution in the photographic study was 0.5 eV also (primary slit = 7 μ) and the exposure time was 4.3 hrs. at 8 KV and 250 ma setting. The densitometer slit height utilized was at the maximum setting of 2.5 mm and the densitometer slit width was 25 μ, which was found to deterioate the photographic resolution by less than 5%(8), i.e., the overall instrumental resolution between photographic and photoelectric detection was roughly equivalent.

Under the above conditions the net line to peak noise ratio for I has been determined to be 63, and for II it is 31 for this particular example. In another photographic study, not shown here, the line to peak noise ratio was 26. Since at this resolution it is possible to obtain a line to peak noise ratio of at least 90 photoelectrically, it appears that photoelectric scans will provide favorable signal to noise ratio values over raw photographic data taken at the same instrumental resolution and exposure time. As shown in Fig. 2, however, the signal to noise ratio of raw digitized photographic data can be improved by averaging out the grain noise. It is also noteworthy that the line to background ratio (L/B) for spectrum I is approximately ten times better than that in II (or III).

However, it is also clear from this study, as well as from another one conducted previously at lower resolution(9), that photoelectric detection, while offering linear response, good line to background ratio values and good signal to noise ratios, is at a disadvantage in terms of total speed of analysis as compared with photographic detection if the wavelength region to be examined is fairly extensive. A preliminary theoretical evaluation of photographic vs. photoelectric detection in the ultra-soft X-ray region has been offered previously.(9) A more rigorous theoretical and experimental evaluation of photographic vs. photoelectric detection capabilities is currently being carried out.(8)

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