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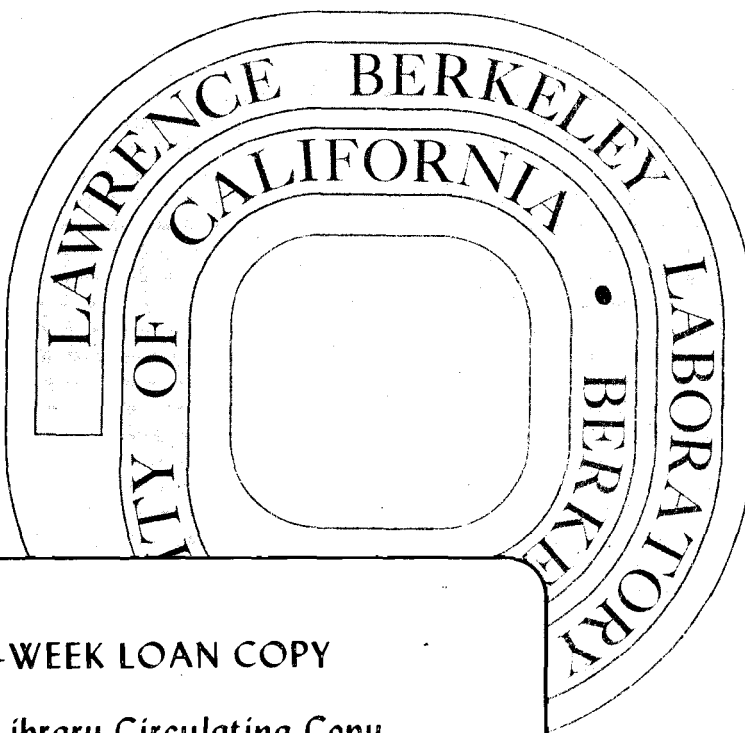
SMALL X-RAY TUBES FOR ENERGY DISPERSIVE ANALYSIS
USING SEMICONDUCTOR SPECTROMETERS

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ABSTRACT

Fast X-ray fluorescence analysis with radioisotope excitation requires intense sources to produce reasonable counting rates. The inconvenience of handling such sources and the small number of suitable radioisotopes places severe limitations on their use.

We have explored the possibility of using low-power X-ray tubes as exciting sources for energy-dispersive fluorescence analysis. The principal advantage to X-ray tubes is the ability to produce X-ray fluxes to three orders of magnitude higher than those obtained with convenient radioisotope sources while dissipating only a few watts in the tube. Furthermore, the variety of possible anode materials and range of currents in the tube make possible optimum choice of exciting energy and intensity for particular applications.

We have designed and tested such tubes in a variety of anode configurations suitable for fluorescence excitation. Using either X-ray filtering techniques or multiple fluorescence geometries it is possible to significantly reduce the Bremsstrahlung background relative to characteristic radiation.

As compared with normal radioisotope-target assemblies, excitation of a sample by the X-ray tube results in comparable sensitivity in only a tenth to one hundredth of the time.

INTRODUCTION

Maximum analytical sensitivity in energy dispersive X-ray analysis is obtained by the efficient excitation and detection of characteristic X-rays in the sample. However, this must be achieved in such a way as to minimize unwanted background in the detector; in most analytical applications using semiconductor spectrometers monoenergetic X-ray excitation is provided by either radioisotope sources or source-target assemblies (1). Although adequate in many applications, radioisotope excitation is limited to a small number of suitable isotopes. Their use for rapid trace analysis is precluded by the difficulties in the handling, storage and replenishment of intense radioactive sources.

We have explored the use of small X-ray tubes as an alternative means of fluorescence excitation with particular emphasis on applications to analysis of trace quantities (down to less than 1 ppm). Their principle advantage is the large characteristic X-ray flux which can be generated with a relatively small expenditure of power input to the tube. For example, an electron current of 1 μA at 27 keV will generate a total of 1.6×10^{10} K X-rays/sec when incident on a copper target (2). This is equivalent to 16 Curies/watt of power input. As the tube voltage, V, is increased the K X-ray intensity increases in proportion to

$(V_o -1)^{1.67}$, where $V_o \equiv V/E_K$ and E_K is the K electron binding energy (2). The X-ray tube output can be varied in energy and intensity by changing the target material and electron current; and, unlike radioisotope sources, an electron beam can be turned off when not in use--an important safety consideration particularly in any large scale applications of the spectrometer systems outside carefully controlled laboratory environments. However, analytical sensitivity, using fluorescence excitation with normal X-ray tubes, is limited by the continuous Bremsstrahlung background generated by the deceleration of the electrons in the anode. Scattering of this spectrum from the sample to detector is unavoidable and a particularly serious limitation when using low-background semiconductor spectrometers (3). In the present work we describe techniques for generating nearly monoenergetic X-ray tube outputs with minimal background interference. Results are presented for both a filtered output X-ray tube and a secondary fluorescence tube.

X-RAY TRANSMISSION TUBE

The simplest method for reducing continuum background is to use suitable X-ray filters to transmit as much of the characteristic radiation as possible while attenuating all other energies. Since any given element is a good transmission filter for its own characteristic X-rays, the anode of the X-ray tube can be made of an appropriate thickness to effectively filter the transmitted X-ray spectrum. Although filtering the spectrum produced at backward angles to the target would achieve the desired result, it proves convenient to employ the transmission

geometry since more efficient anode to sample spacings are possible and the use of multiple targets is facilitated. Further filtering can be included to selectively reduce the Kβ intensity and more closely approach a monoenergetic X-ray beam.

Table 1 is a summary of relevant X-ray data for elements of interest in this discussion. One point of immediate importance is that the half-thickness for characteristic X-ray absorption is of the order of 10^{-3} cm for all elements. This is a convenient value since a filter thickness of 3 to 5 half-thicknesses provides both adequate X-ray transmission and sufficient heat conduction to dissipate the incident power into the anode support.

A scale drawing of the X-ray tube is shown in Fig. 1. The electron beam is obtained from a tungsten filament and the current can be controlled either by the filament power or with the intermediate electrode voltage. The beam is focused on the target anode which is held at the high positive voltage and supported by the ceramic insulator. (Operation of the anode at positive voltage instead of ground potential is dictated mostly by convenience of design. There are possible advantages to operation at ground potential since the exit window may then also be the transmission target filter; thus affecting higher geometric efficiency.) Optimum filter thickness is determined empirically but 3 to 5 half-thicknesses of the target material are nearly optimum. A portion of the total filter thickness is mounted external to the tube to eliminate unwanted characteristic X-rays from the stainless steel vacuum enclosure.

TABLE I

| Element	Z	K Absorption Edge (keV) *	Kα Energy (keV) *	Kβ Energy (keV) *	Half-Thickness at Kα Energy (cm) †
Al	13	1.560	1.486		6.1×10^{-4}
Ti	22	4.965	4.508	4.931	1.4×10^{-3}
V	23	5.464	4.949	5.426	1.2×10^{-3}
Fe	26	7.111	6.398	7.057	1.2×10^{-3}
Ni	28	8.332	7.471	8.263	1.3×10^{-3}
Cu	29	8.980	8.040	8.904	1.5×10^{-3}
Zr	40	17.999	15.744	17.704	5.3×10^{-3}
Mo	42	20.004	17.441	19.651	3.7×10^{-3}
Rh	45	23.220	20.165	22.777	3.5×10^{-3}

* See Ref. (6)
† See Ref. (7)
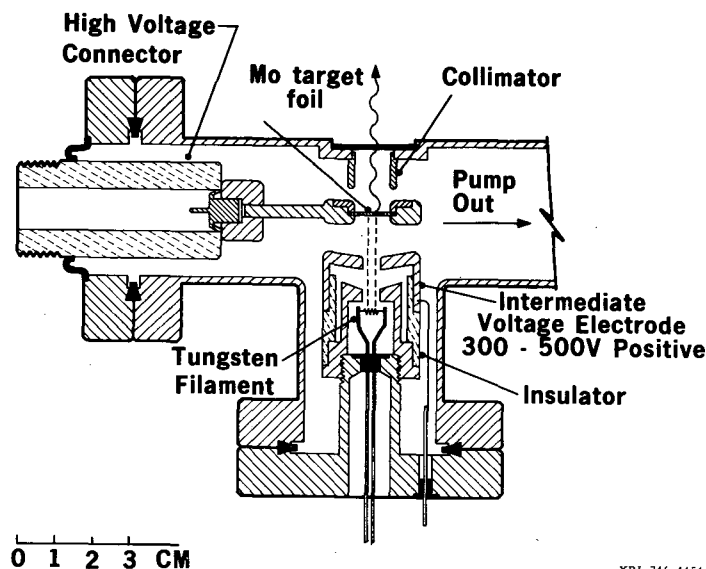
Figure 1. Schematic of transmission X-ray tube.

Most of the present data were obtained with molybdenum target and total filter thickness of 0.012 cm. The tube was operated at 42 keV with variable currents up to 500 μA. The maximum beam power of 25 watts was dissipated mostly by radiation from the anode structure. Although increasing the beam voltage would result in improved characteristic X-ray yield relative to Bremsstrahlung, a practical limit is set by the transmission of the high energy continuum Bremsstrahlung X-ray through the filter. Using a voltage regulated filament supply, the tube output was stable to within ± 10% over several hours; however, we anticipate providing feedback stabilization in the near future.

Figure 2 is a comparison of fluorescence spectra obtained using radioisotope excitation and transmission X-ray tube excitation for the case of a biological sample. The spectra were obtained using a low-background guard ring reject system (3) and pulsed-light feedback electronics (4); only the high energy portions are shown since there is no significant difference in background at lower energies. The radioisotope source-target assembly employed a 125 millicurie ^{125}I source and molybdenum target with a separation of 1 cm between the source and molybdenum target, and 1 cm between the molybdenum target and the sample. The X-ray tube anode filter was 0.012 cm molybdenum and gave a ratio of 30:1 for the Kα X-ray peak height-to-background height just below the Kα peak in the tube output spectrum. With the X-ray tube operating at 100 μA and 42 keV the spectrum was acquired in approximately 15 minutes at a total counting rate of 4000 cts/sec Trace elements concentrations for the 0.3 mm thick sample were obtained by the method described in Ref. (5). With a 500 μA beam current and the anode to sample distance of 8 cm as used in these measurements, the counting rate was 50 times that obtained with the radioisotope source.
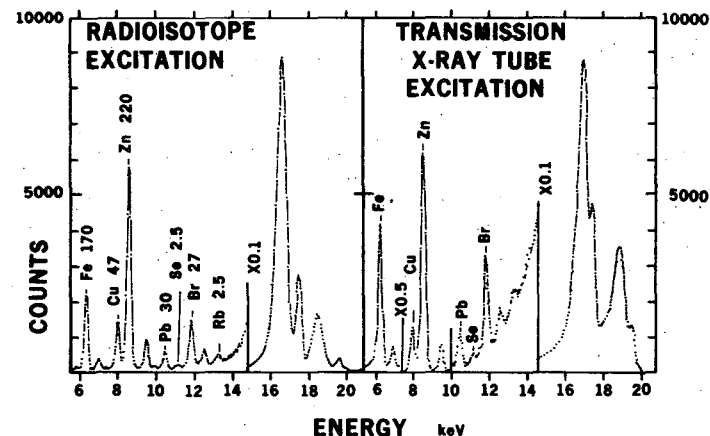
Figure 2. Comparison of excitation modes showing spectra obtained from biological specimen (lyophilized horse liver). Numbers on peaks indicate concentrations in ppm for the sample pellet.

A further improvement in excitation efficiency could easily be realized by decreasing the anode-sample and sample-detector geometry. It is apparent from Fig. 1, that relatively simple mechanical modifications could be made to decrease these distances to affect an efficiency improvement of at least 10 times. Looking at the spectrum obtained with the transmission tube, one sees that it should be possible to obtain sensitivities of substantially better than 1 ppm in a few minutes at counting rates limited only by the detector electronics. (For a more detailed discussion of detection limits see Ref. (3).)

An interesting feature of the data is the difference in the ratio of backscatter peak height to fluorescence X-ray intensity between the two spectra. Although a part of this difference can be accounted for by the lower peak to background in the X-ray tube output spectrum, most of the difference is due to the difference in source-sample-detector geometry. In the source-target assembly the average scattering angle for the molybdenum X-rays is near 180° whereas the X-ray tube is mounted horizontally with a total scattering angle of approximately 90°. These angles are the respective maximum and minimum in the incoherent scattering differential cross section. These conclusions are supported by data obtained with the secondary fluorescence tube operated in a similar geometric configuration.

SECONDARY FLUORESCENCE X-RAY TUBE

A substantial further reduction in continuum background can be realized by using a secondary excitation mode analogous to the source-target arrangement. The X-rays generated in the anode by the electron beam are made to strike a secondary target--the characteristic X-ray from this target then are used to excite X-rays from the sample. Although this conversion process results in a reduction in X-ray output for a given electron beam power, it virtually eliminates the continuous background in the output spectrum. Since the secondary target need not be an electrical conductor or dissipate large amounts of power, it is possible to generate characteristic X-rays from elements not available as metallic foils.

The choice of anode-secondary target combination is determined by choosing an anode material with Kα X-ray energy as near as possible to the maximum photoelectric cross section for the secondary target. Referring to the data in Table 1, it is apparent that the rhodium to molybdenum anode target combination is especially fortuitous in this regard. In fact the total conversion efficiency of rhodium to molybdenum X-ray is 0.52--i.e. for every rhodium Kα X-ray incident on a thick molybdenum target, 0.52 molybdenum K X-rays are generated isotropically. The total efficiency for secondary fluorescence excitation is then determined principally by the solid angle subtended by the secondary fluorescence target relative to the anode.

In Fig. 3 is shown a schematic of an experimental tube used for secondary fluorescence target excitation. Electrons emitted from the filament are accelerated into the annular rhodium anode through a series of openings in the molybdenum secondary target. The collimator shields the external sample from the rhodium anode but not the molybdenum target. The geometric efficiency of the rhodium to molybdenum conversion is approximately 3 to 5% yielding an output rate approximately 0.1 times that of the transmission X-ray tube for a given beam power. (The reason that the difference is not larger is due to the less than 10% X-ray transmission through the 0.012 cm filter in the transmission tube.) It is possible to increase the rate further by operating at a higher anode potential since transmission of Bremsstrahlung through the filter is no longer a problem--in the present series of measurements the potential was limited to 45 keV only by the high-voltage connector rating.
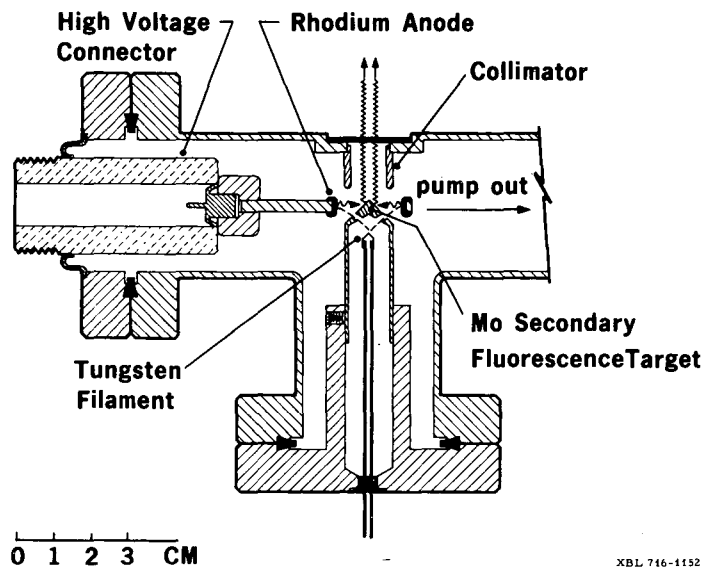
Figure 3. Schematic of secondary fluorescence tube with rhodium anode and molybdenum secondary target.

Direct measurement of the output spectrum show a ratio of peak-to-background height of greater than 300:1. Figure 4 is a comparison taken with radioisotope excitation similar to that shown in Fig. 2. The improved peak-to-background of the bromine peaks compared to the transmission tube reflects the improved quality of the secondary fluorescence input spectrum. The differences between the transmission tube and the radioisotope excitation are small. The greatly enhanced ratio of coherent to incoherent scattering intensity in the spectrum obtained with the X-ray tube has been attributed to the fact that the

beam was more widely divergent at the sample due to a closer geometry employed with the particular tube used. This allowed a larger number of small angle scattering events to reach the detector thus enhancing the coherent contribution.
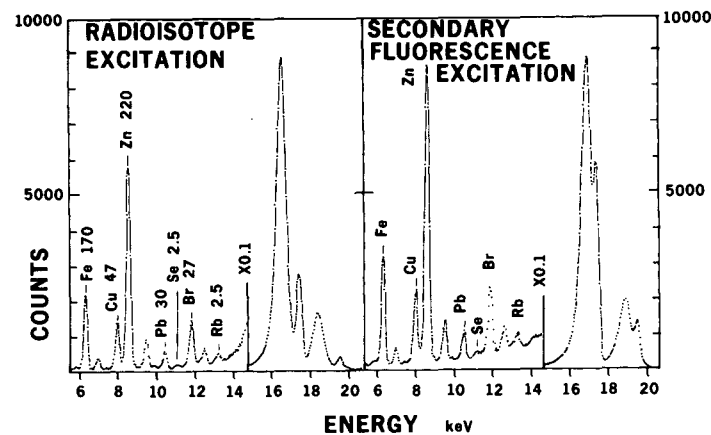

Figure 4. Comparison of excitation modes using same sample as Fig. 2.

SUMMARY AND CONCLUSIONS

Measurements performed with electron beam excited X-ray sources have deomonstrated their greatly increased counting rate capability relative to radioisotope excitation; techniques for eliminating continuum background have minimized degradation in analytical sensitivity when using X-ray tube excitation. Although the peak-to-background

ratio with the transmission X-ray tube was considerably worse than that possible with secondary fluorescence, it has the advantages of higher X-ray output flux and simplicity of design. Other potential advantages not exploited in the present work are improved geometrical efficiency with the anode held at ground potential and possible multiple anode operation with electronic switching between targets. The secondary fluorescence tube is characterized by greater peak to background, but a lower efficiency for X-ray production; an additional advantage being the potentially greater flexibility in secondary target material.

Although we have emphasized the example of molybdenum X-ray sources, tubes with a variety of other materials including copper, nickel and zirconium have been operated. Experience with heavier element targets has been limited primarily due to the lack of suitable high voltage connectors. In addition to extending the measurements to higher energy X-ray sources, it is also possible to conceive of a variety of different mechanical improvements which could improve geometric efficiency. In particular one can conceive of secondary fluorescence tubes with an annular target similar to the source-target assembles or small diameter transmission tubes for improved geometries. However, our experience has indicated that count rates obtained with existing designs are adequate for most present analytical applications. As further discussed in Ref. (3) and (5), the combination of low-background semiconductor spectrometers and monoenergetic X-ray tube excitation provides a new and useful tool for multielement analysis.

ACKNOWLEDGMENTS

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