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BANGLADESH ATOMIC ENERGY COMMISSION

**OPTIMIZATION OF TUBE PARAMETERS IN A TUBE
EXCITED X-RAY FLUORESCENCE (TEXRF) SYSTEM
USING SECONDARY FLUORESCERS**

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A. Islam and S.K. Biswas

Chemistry Division
Atomic Energy Centre, Dhaka

Abstract

A study on the optimization of excitation parameters in a tube excited X-ray fluorescence system (TEXRF) having Mo as the primary target has been carried out for biological matrix. Fe, Zn and Mo were used as the secondary fluorescers. For the present investigation a cellulose based synthetic standard containing K, Cr, Ni, Zn, Se and Y was excited with the TEXRF system. All experiments were carried out under the same experimental conditions except the tube potential. For each fluorescer the minimum detection limits (MDL) of excited elements were calculated for the corresponding tube voltage. The MDLs were found to be increasing with decreasing atomic number and it was also observed that the maximum sensitivity with Fe and Zn secondary fluorescers for elements analyzed occurred around 35 kV of the excitation potential. For Mo secondary fluorescer maximum sensitivity was found at higher excitation potential. In most cases MDLs were minimum at 40-45 kV of the excitation potential.

Introduction

The sensitivity of an instrumental analytical system depends on a number of parameters or factors. In many cases, a small change in any of these parameters may cause a significant effect in the efficiency of the system. A parameter must have a specific value under which the system can work in an optimal manner. Hence, the effective utilization of the strength of an analytical method requires the optimization of the parameters involved.

The X-ray fluorescence (XRF) technique is perhaps one of the leading analytical tools widely used for multi element analysis in a variety of matrices. Many laboratories all over the world are using the technique for different analytical measurements on routine basis, because the method is fast and needs minimal or no sample preparation which in turn avoids the possibility of contamination. The sensitivity of the tube excited XRF technique is a function of several factors including excitation conditions^{1,2}, specimen conditions, the geometry of the experimental setup, the detector and the data acquisition system. For a particular experimental condition and for a specific sample all factors except the excitation conditions are fixed. In TEXRF analysis using a given experimental condition, the X-ray yield of an element varies greatly with the change in excitation parameters of which the tube potential is the most important³. An useful expression relating the x-ray intensity in the continuum to excitation conditions³ is:

$$I_{\text{int}} = (1.4 \times 10^{-9})iZV^2 \quad (1)$$

where

I_{int} = Integrated intensity of the continuum

Z = Atomic number of the X-ray tube target

i = X-ray tube current,

V = X-ray tube potential

The Equation (1) shows the effect of X-ray tube current, potential and target on the continuum. The factor $(1.4 \times 10^{-9}) ZV$ in the Equation (1) may be regarded as the efficiency factor of a X-ray tube operated at an input power iV watts. The x-ray tube potential has by far the most marked effect. The X-ray yield of an element from a sample bombarded with the primary x-rays as well as its background depends on the intensity of the continuum which, in turn, depends on V , i , and Z . The lower the background the lower the detection limit (MDL) and this can be achieved through the optimization of the tube parameters.

In X-ray spectrochemical analysis, there are different ways of excitation of characteristic X-ray spectra. The methods of excitation are classified as the primary or secondary depending on whether excitation is by primary photons from the X-ray tube or excitation by secondary X-ray beam from the secondary fluorescers respectively. The excitation by primary beam has several drawbacks. It is not monochromatic but consists of the continuum and the line spectrum of X-ray tube target element. Only that part of the primary beam having energy higher than the absorption edge of an element contributes to the excitation of the spectrum of that element. Although the continuum provides the principal source of specimen excitation, it also generates background which in turn affects the sensitivity of the system. On the other hand, the excitation by tertiary beam originating from the secondary fluorescer is very efficient. It consists of the characteristic X-rays originated from the fluorescer used and almost free from continuum and other scattered radiations. Thus, if a suitable secondary target element (fluorescer) is used for

the analysis of the required elements (having absorption edges lower than the energy of the secondary beam from the fluorescer), then better detection limits can be obtained.

Although the primary beam provides the principal source of background, it can be used profitably for excitation in many practical cases. It has a great advantage when lighter elements are excited by its low energy bremsstrahlung. Since, the present experimental setup does not have the facility for primary excitation, the proposed investigation is limited to secondary excitation only. The samples were irradiated by secondary X-rays from a target element (fluorescer) having a strong spectral line at energy higher than that of the analyte absorption edge; such secondary targets are themselves excited by the primary X-rays from the X-ray tube.

The ideal way of optimization of the tube parameters (i.e., excitation potential and current) would be to find the optimum input power (tube potential and current pair) where one could obtain the best sensitivity for a given matrix. For such a study the input power (IV) of the tube should be constant through out the experiment. Since the X-ray tube potential (V) is the most significant factor for the spectral distribution pattern of the primary beam, the objective of the present work is to study the sensitivity of different analytes as a function of the tube potential of a X-ray tube in a tube excited X-ray fluorescence (TEXRF) system using different secondary fluorescers for elemental analysis in biological matrices. The tube current was kept constant based on the facts that it has effects only on the intensity of the primary beam but not on its spectral distribution which have marked effects on the efficiency of excitation of the characteristic X-rays from the sample. This is also more practical to change the voltage frequently but not the current from the instrumentation point of view.

Experimental

Sample preparation

In connection with the present investigation a multi element standard sample containing K, Cr, Ni, Zn, Se, Y was synthesized using chromatographic grade Whatman cellulose as the matrix. A standard solution of each of the added elements was prepared. A suitable portion from each of the prepared standard solutions was then added in 6 g of dry cellulose powder contained in a platinum crucible whose weight was taken earlier. The whole cellulose powder was immersed by the total volume of the added portions of the standard solutions. The solution was evaporated to dryness in a water bath. The sample was then dried under an IR lamp at about 70° C until a constant weight was found. The whole mass was transferred into a aluminum carbide mortar. About 3 ml of methanol was added into the mortar and mixed in order to ensure the uniform spreading of the added elements in cellulose. The sample was finally dried and ground into a fine powder with a pestle. A blank sample was also processed in the same way as the standard. The prepared sample was put into a polythene container and preserved in a desiccator until it was further processed for analytical purpose. It is to be mentioned that cellulose was made into powder by heating it at 120° C for about 2 hours.

For irradiation, 1 g of standard sample was pressed (2 tons/sq. inch) into a pellet of 1 inch diameter with a pellet maker (SPECAC) and preserved in a desiccator.

Excitation of the sample

The experimental setup used for the present study was composed of a X-ray generator (Siemens/Kristalloflex 710 H) having Mo tube (Max. power 2000 W), an Ortec Si(Li) detector with a preamplifier, a Canberra 1024 channel multichannel analyzer and a Canberra 2020 amplifier. Detector characteristics were as follows: resolution, 170 eV at 5.9 keV; active area, 30 mm²; beryllium entrance window thickness, 25 μm. The schematic diagram of the experimental setup is shown Fig.1. For secondary excitation, the fluorescers used were Fe, Zn and Mo. The primary X-ray beam coming from the X-ray tube was allowed to hit the secondary fluorescer to produce secondary X-rays which were directed towards the sample (pellet) placed at 45° to the incident beam. The characteristic X-rays of the elements in the sample were detected by the Si(Li) detector positioned below at 90° to the incident beam. The spectra were collected by the multichannel analyzer. The optimum excitation potential (kV) was investigated by irradiating the sample under a range of tube potentials from 25 to 50 kV at a constant tube current using Fe, Zn and Mo secondary fluorescer under the same experimental condition. The tube current was fixed at 25 mA based on the conditions that for maximum tube voltage (50 kV), the dead time for the collection of spectra remained within the reasonable limit (<5%) for all the secondary fluorescers used in the work. The blank was also irradiated under identical condition as the sample. The spectra generated at different tube potentials (25 kV, 30 kV, and 45 kV) for Mo fluorescer are shown in the Fig. 2.

Data processing

The spectra collected in the analyzer were transferred to an IBM compatible 386 computer. The spectral data were evaluated using a software, AXIL (analysis of X- Ray

spectra by iterative least squares) for net area under each photo peak representing an element.

Determination of minimum detection limit (MDL)

Considering the statistical errors in counting, the MDL is defined as the amount of an element in ppm which yields an X-ray intensity equal to 3σ of the background under the peak in an interval equal to the FWTM (full width at tenth maxima) of the peak. The σ is given by:

$$\sigma = \sqrt{\{(\text{Background/channel}) \times \text{FWTM}\}} \quad (2)$$

Determining the value of FWTM from the peak of each element using the analyzer programme the 3σ was calculated using the equation (2). The MDL of each element was then calculated from the value of 3σ , the concentration and the net counting area of the element according to the expression⁴ given below:

$$\text{MDL} = (3\sigma/N) \times \text{conc.} \quad (3)$$

where, N = Net area (net counts)

The spectrum of the blank sample did not show the presence of any element with a appreciable net area for correction.

Results and discussion

For Fe, Zn and Mo fluorescers, the observed MDL values of the excited elements were plotted against the corresponding tube potentials. The plots are shown in the Figs 3 and 4.

Variation of MDL with atomic number (Z)

It is seen in the Fig.3 that for Fe fluorescer the MDL increases with decreasing Z and the maximum atomic number of element excited is 24 corresponding (Z-2) of the fluorescer. For Zn fluorescer the MDL also increases with decreasing Z and the Ni, the highest atomic number element corresponding Z-2 of the fluorescer is excited. It is observed from Fig. 4 that for Mo fluorescer, the MDL also increases with decreasing Z number and the element with highest atomic number corresponding Z-3 of the fluorescer excited for K X-rays is Y. The only L X-ray excited in the present study was from Pb.

Variation of MDL with excitation voltage

The calculated MDLs for different elements with the above described experimental setup using three different secondary fluorescers have been plotted against the corresponding excitation potential of the primary beam and they are shown in Fig. 3 and 4.

It is known that the I_{max} of the continuum shifts toward higher energy with increasing excitation potential. The intensity of the secondary X-rays emitted from the

fluorescer increases as the I_{\max} approaches the absorption edge of the fluorescer used. Around a certain potential, the fluorescer emits X-rays with maximum intensity which starts to decrease as the potential is further increased, as the I_{\max} shifts to a higher energy which is not effective for excitation. The intensity of characteristic X-rays of the analyte element increases with the increasing intensity of the secondary X-rays from the fluorescer and the lowest value of MDL of the analyte is obtained when the X-rays from the analyte is excited with maximum intensity.

Fig. 3 shows that the lowest MDL occurs around 35 kV of the excitation potential for most of the elements analyzed using Fe and Zn as the fluorescers. It appears from the experimental results that for Fe and Zn secondary fluorescers 35 kV could be the optimum excitation potential for best sensitivity.

In Fig. 4, it is shown that for the Mo fluorescer, the lowest value of MDL occurs at 40 kV for Ni and Zn. The same occurs at 45 kV for Se and Y. The lowest MDL value for Pb L-line was observed at 35 kV of the excitation potential. Like Fe and Zn fluorescers, the Mo fluorescer also excites the characteristic X-rays from the sample depending on the spectral distribution (I_{\max}) of the primary beam affected by the excitation potential applied. It is evident from the Fig. 4 that for practical samples 40-45 kV excitation potential would be the best when Mo is used as secondary fluorescer.

Conclusions

The study of the excitation of characteristic X-rays in connection with the elemental analysis in biological matrix by the TEXRF system with Mo tube shows that a tube potential of 35 kV should be applied when Fe and Zn are used as the secondary

fluorescers under the present geometry of experimental setup, detector and the data acquisition system. For the Mo secondary fluorescer, a higher excitation potential of 40-45 kV has been found to give better sensitivity.

Acknowledgement

The authors would like to thank Dr. S.A. Tarafdar, Head, Chemistry Division, AECD for his continuous encouragement throughout the work. The valuable suggestions of Dr. M. Khaliqzaman, Head, Accelerator Facilities Division, AECD and professor A.H. Khan, Chemistry Department, Dhaka University on the work are thankfully acknowledged. The continued support from Dr. Md. Sanaullah, Director, AECD is greatly appreciated. The cooperation of the staff members of the Chemistry Division is acknowledged with gratitude.

References

1. P.J. Potts, P.C. Webb and J.S. Watson, X-ray Spectrom, 13 (1984) 2.
2. C. Freiburg, W. Rechert and A.G. Solomah, X-ray Spectrom, 15 (1986) 155.
3. Eugene P. Bertin, Principles and Practice of X-ray Spectrometric Analysis, Plenum Press, New York-London, Edi. 2, p. 17-18., 1975.
4. D.B. Bilbrey, D.J. Leyland and D.E. Leyden, X-ray Spectrom. 16 (1987) 151.
5. P. Wobrauschek, P. Kregsamer, C. Strelj and H. Aiginger, X-ray Spectrom., 20 (1991) 23.

Figure Captions

1. A schematic diagram of the tube excited X-ray fluorescence (TEXRF) system with detection geometry.
2. The spectra of the same standard sample excited at different tube potentials using Mo secondary fluorescer under the same experimental condition.
3. The MDL as a function of excitation potential for Fe and Zn secondary fluorescers.
4. The MDL as a function of excitation potential for Mo secondary fluorescers.

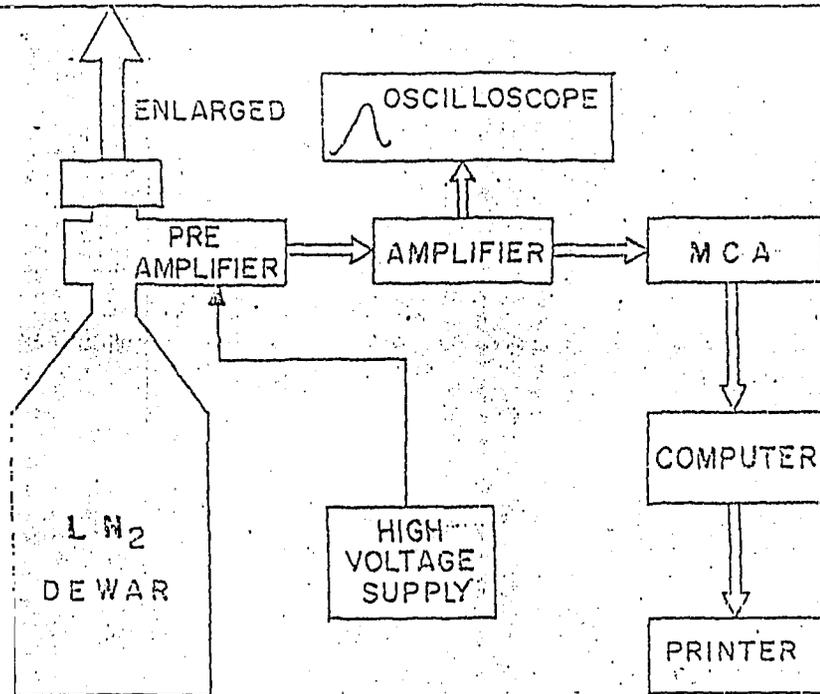
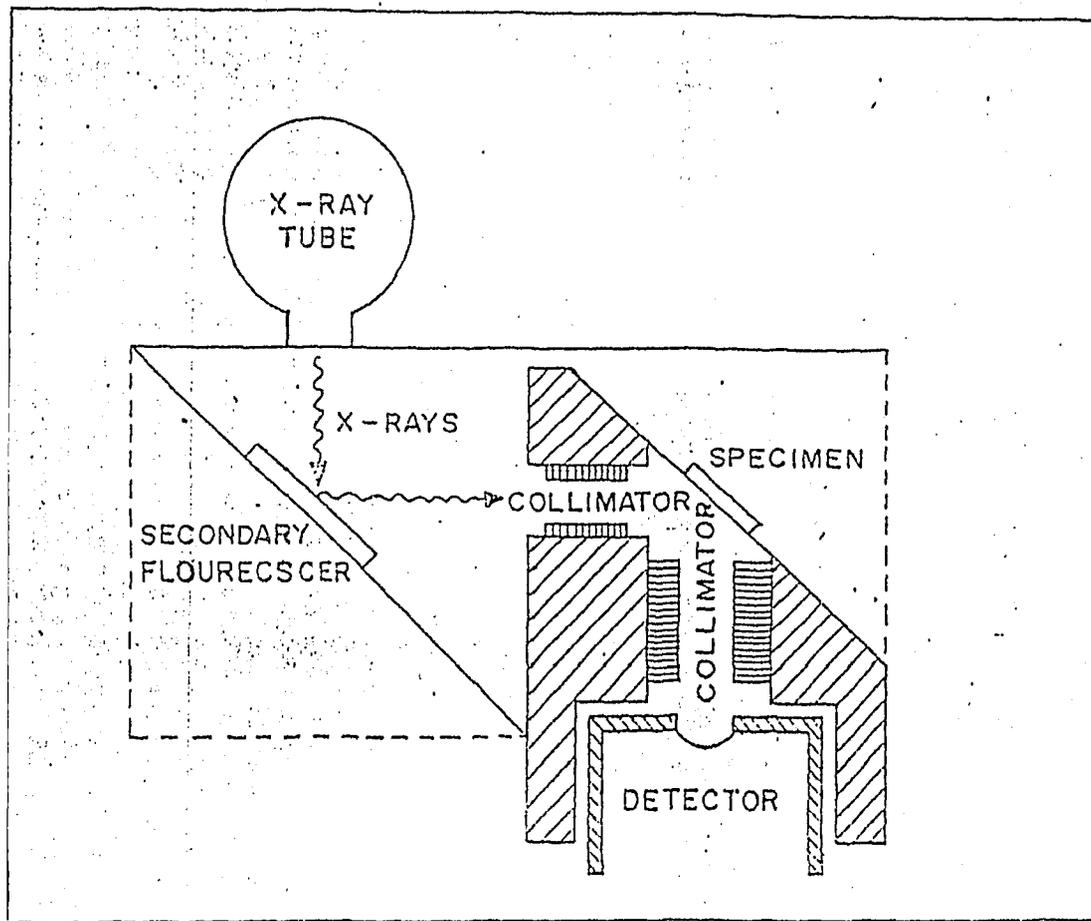


Fig. 1

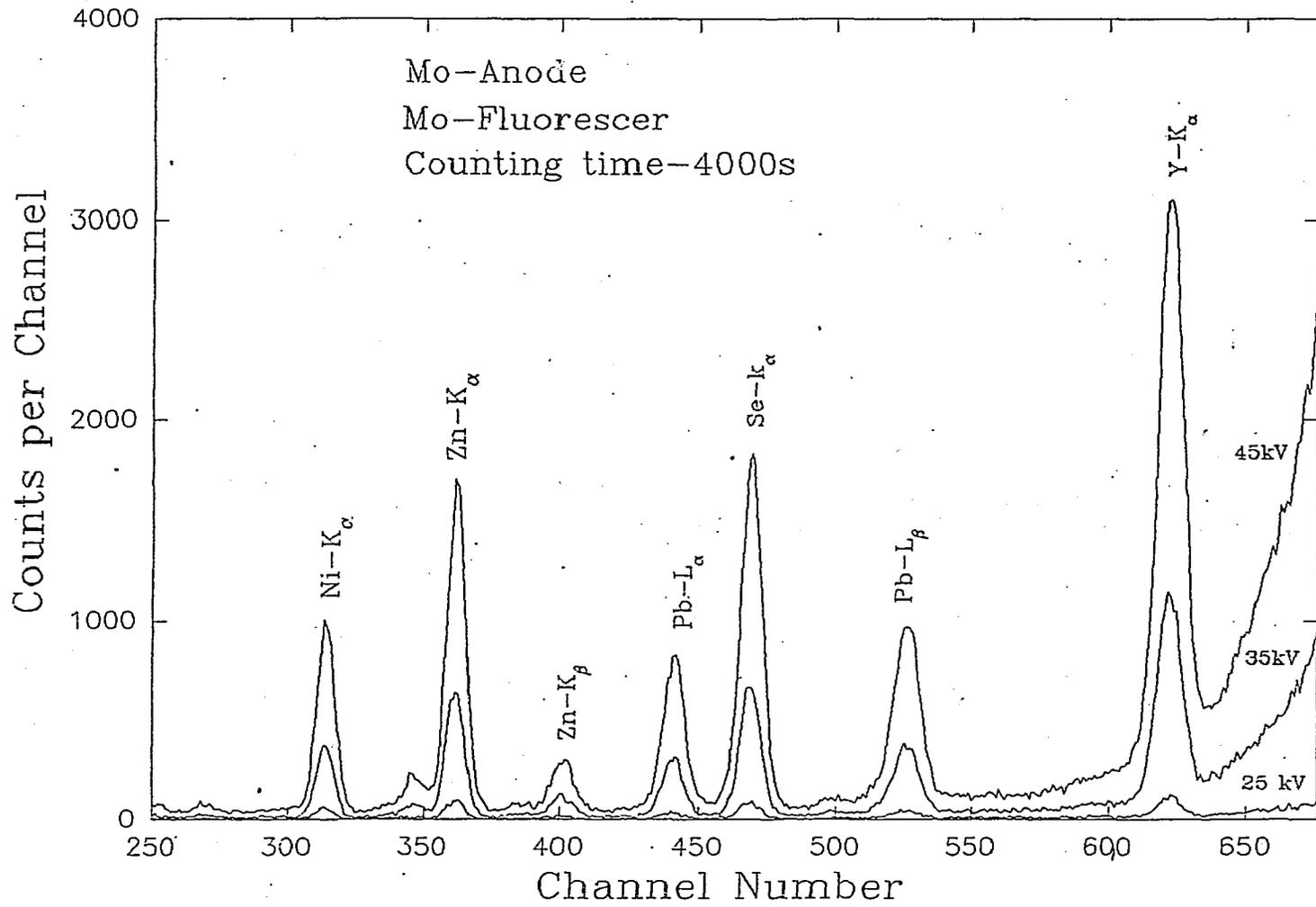


Fig. 2

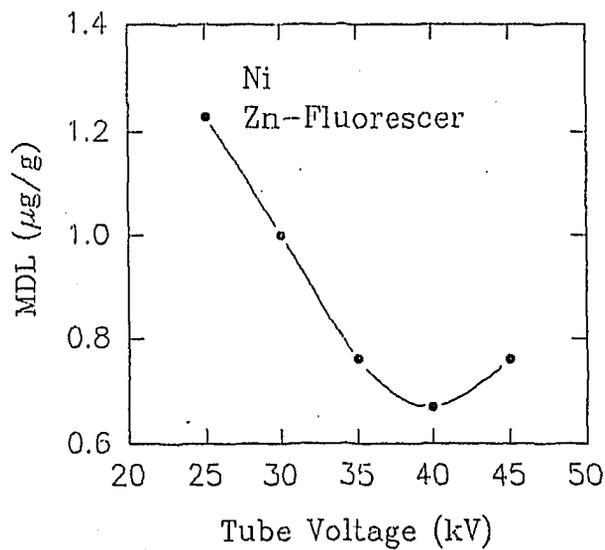
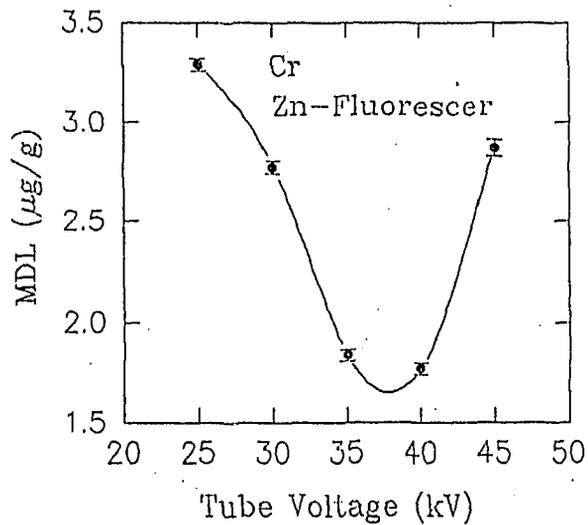
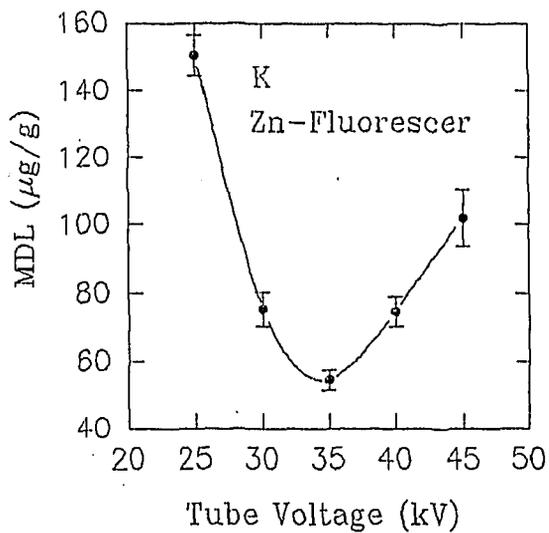
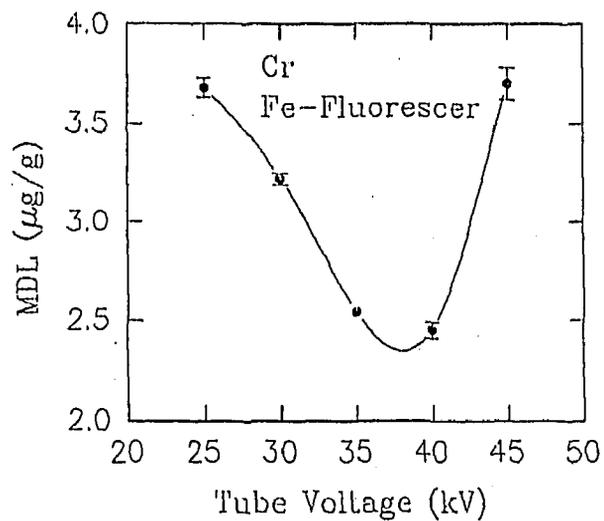
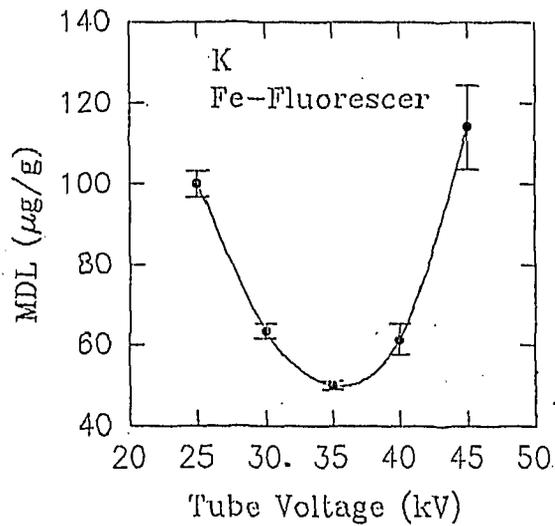


Fig. 3

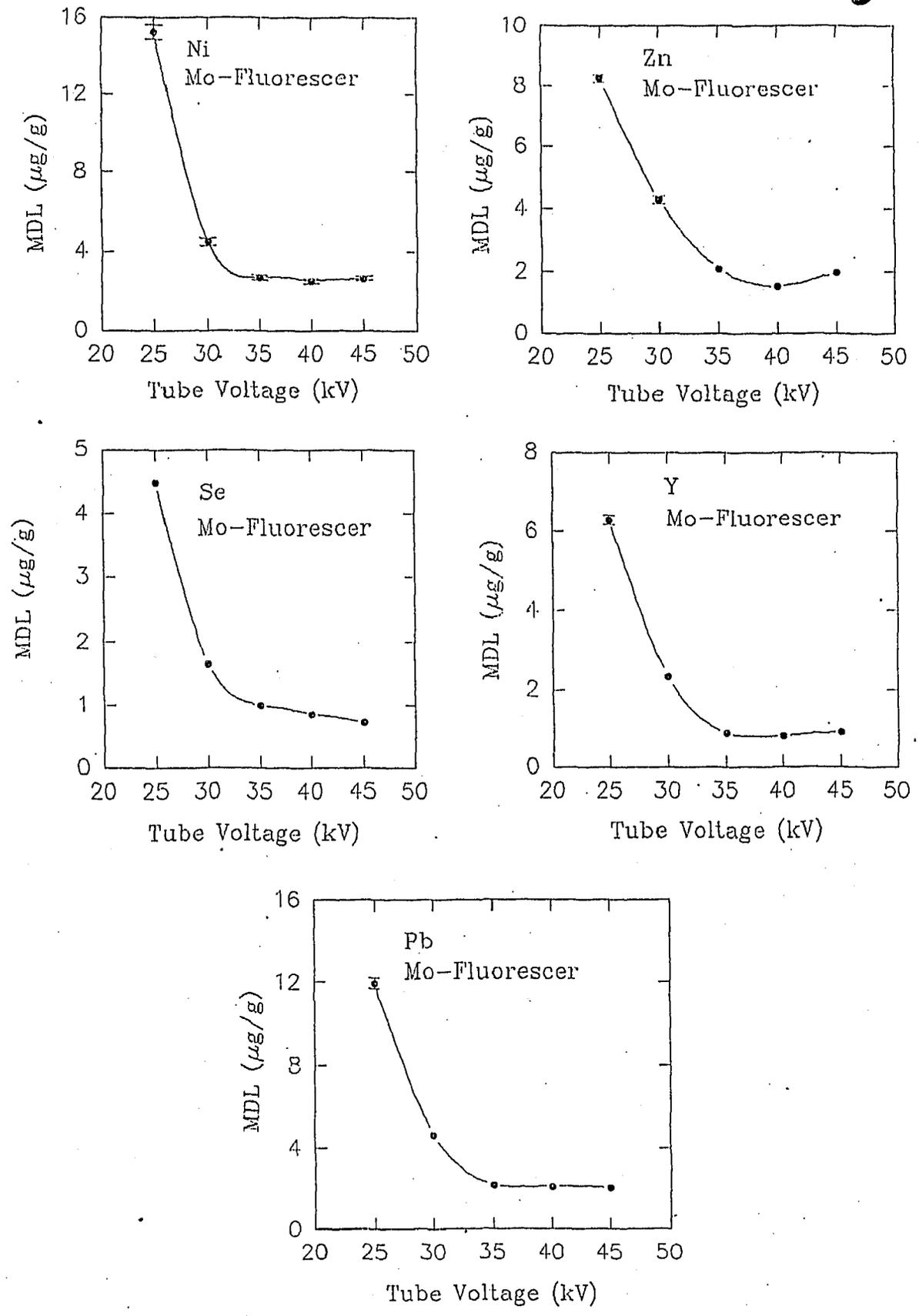


Fig. 4