Title
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Publication Date
1976-05-01

Presented at the Proceedings of the ERDA
Symposium on X- and Gamma-Ray Sources
and Applications, Ann Arbor, MI,
May 19 - 21, 1976

LBL-5352

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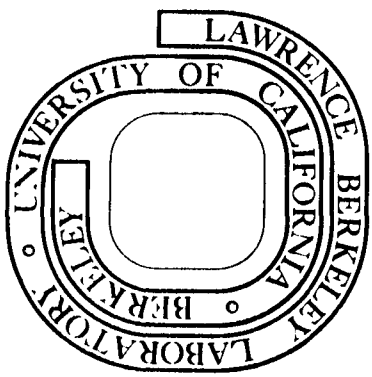
May 1976

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48



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EXCITATION METHODS FOR ENERGY DISPERSIVE ANALYSIS*

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ABSTRACT

The rapid development in recent years of energy dispersive X-ray fluorescence analysis has been based primarily on improvements in semiconductor detector X-ray spectrometers. However, the whole analysis system performance is critically dependent on the availability of optimum methods of excitation for the characteristic X rays in specimens. A number of analysis facilities based on various methods of excitation have been developed over the past few years. This paper discusses the features of various excitation methods including charged particles, monochromatic photons, and broad-energy band photons. The effects of the excitation method on background and sensitivity will be discussed from both theoretical and experimental viewpoints. Recent developments such as pulsed excitation and polarized photons will also be discussed.

INTRODUCTION

Over the past several years the level of activity in the area of energy-dispersive analysis has increased dramatically. Much of this work has involved applications in environmental research and monitoring where the capabilities of the energy dispersive methods closely match the analytical requirements.[1] These capabilities include the accurate multiple-element, non-destructive analysis of large volumes of samples at a reasonable cost.

Modern energy-dispersive analysis using semiconductor detector spectrometers is made feasible by the improvements in electronic energy resolution,[2] detector background characteristics,[3] and system counting rate performance[4] which occurred in the years before and immediately following the previous 1970 conference in this series.[5] More recently, however, development in these areas have been less dramatic and only minor improvements in energy resolution have been reported in the past few years. On the other hand, there has been a considerable amount of recent research into the design of complete analytic systems including the optimization of the excitation method for particular types of applications. These methods now include heavy charged particles,[6-8] continuous photon sources,[9] and discrete energy photon sources.[10,11] These radiations can be derived either from radioisotope sources or from particle accelerators and X-ray tubes. In many applications where a high sensitivity or large sample throughput are required, the latter methods are preferred over radioisotope sources due to the higher counting rates which can typically be achieved.

To apply these various techniques to a given problem it is important to understand the basic difference between the spectral data obtained in each case. The goal of the present paper is to present a quantitative description of the basic physical processes operating in each of the excitation methods and to relate this to the spectral response in each case. Estimates for the sensitivity and limits of detection can subsequently be calculated.

Spectra will be calculated using simple theoretical models and empirical data where necessary. Although the calculations are of necessity approximate, it is hoped that the description of the interactions and their effect upon the final spectrum will serve to ellucidate the basic differences in the methods and provide a basis for comparison between them in a given application. Experience has shown that even relatively simple calculations can provide accurate representations of the experimental response of the complete analytical system.

CALCULATIONS

The calculations assume a simplified sample form as shown in Fig. 1. It consists of a 25 mg/cm^2 carbon substrate on which has been deposited 250 ng/cm^2 of the elements Al, S, Ca, Fe, Cu and Br. This corresponds to the type of sample obtained by deposition on a typical cellulose fiber filter and is of the same areal density as a very thin biological specimen. If the elemental deposits were uniformly distributed through the substrate the concentrations would correspond to 10 ppm by weight.

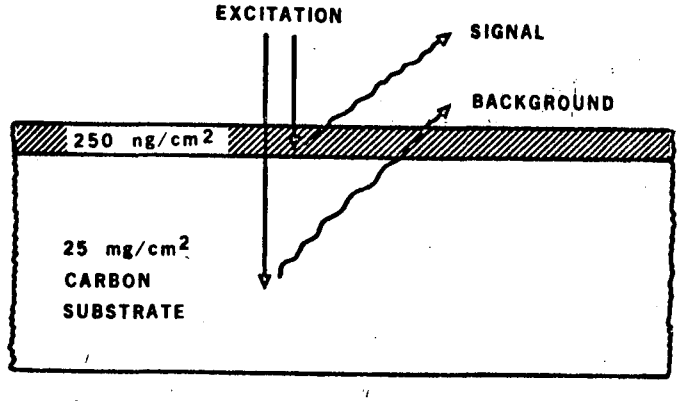

Fig. 1. Schematic of the idealized sample form used in the calculations.

* This report was done in part with support from the United States Environmental Protection Agency under interagency agreement with the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

This form of sample was chosen for consideration since the trace element type of measurement represents a more challenging problem from the point of view of sensitivity and detectability. It more closely approximates the typical samples enoucntered in air pollution and biological analysis. Finally, the sample form in Fig. 1 represents the most easily calculable since one can validly make a number of simplifying approximations.

The calculations assume that the signal originates from interactions in the surface layer only and that energy loss or attenuation effects in this layer are negligible. The background radiation observed in the detector is caused by the interaction of the exciting radiation in the 25 mg/cm^2 substrate. Enhancement effects between the two layers and absorption within a layer are neglected.

Four types of fluorescence excitation will be considered: a) direct electron bombardment, b) charged particle excitation with 3 MeV protons, c) monoenergetic photon excitation, and d) continuous photon irradiation. The spectral data are calculated assuming an energy resolution of 200 eV full width at half maximum (FWHM) independent of X-ray energy.

Direct Electron Excitation

Although it is not readily used for routine X-ray fluorescence analysis of large samples, direct electron excitation is included in the comparison because of its importance in electron-probe devices. The dominant feature of electron excited spectra is the continuous Bremsstrahlung background generated by the electrons as they are slowed down in the electrostatic field of the atoms in the substrate. Fluorescent X rays result from the direct vacancy production in the atoms in the surface layer.

Although very detailed calculations of these effects are available in the electron probe literature, the results shown in Fig. 2 are based on an earlier X-ray production model.[12] It is assumed that the 20 and 40 keV electrons are completely stopped in the substrate and produce a continuous spectrum described by:[12]

$$N(E) = 2.76 \times 10^{-6} Z \frac{(E_o - E)}{E} \Delta E \qquad (1)$$

where N(E) is the number of quanta of energy E in the interval ΔE, E_o is the energy of the electron beam, and Z is the atomic number of the target. The ionization cross sections are calculated assuming a full energy electron beam with no corrections for energy loss in the thin deposited layer. The low-energy X-ray spectrum is attenuated by a 50 μm Be window. This accounts for the steeply sloped background at low energies and the subsequent difficulty in detecting the Al signal. A more rigorous treatment would include the effect of X-ray absorption in the substrate resulting in a reduction in background at very low energies.

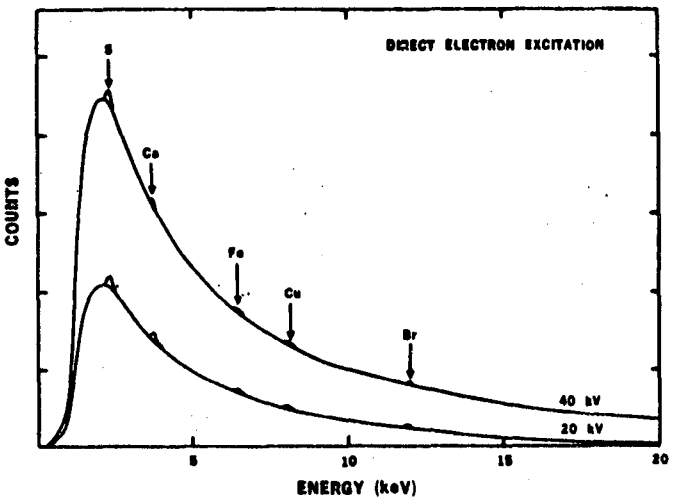

Fig. 2. Calculated spectra assuming 20 keV and 40 keV electron excitation.

Charged Particle Excitation

Fluorescence measurements using heavy-charged particles such as protons or alpha particles are expected to be much more sensitive than electron excitation. The cross section for Bremsstrahlung production is reduced by several orders of magnitude due to the increased mass of the particles.[13] The dominant spectral background no longer results from direct Bremsstrahlung production but is due to continuum radiation emitted in the slowing down of secondary electrons produced in the sample. Heavy particles are very efficient at producing ionization in light elements resulting in a sizeable number of energetic electrons which have been ejected from the inner atomic shells in the substrate. These produce a continuum photon distribution whose endpoint energy is determined by the maximum energy transfer to the electrons by the heavy ionizing particles. The energy of the charged particle beams are normally limited to 3 MeV for protons and 16 MeV for alpha particles in order to achieve optimum sensitivity.

Very successful models have been developed to describe ionization by heavy-charged particles including expressions for the energy distributions of the ejected inner shell electrons. These results have been combined with the appropriate Bremsstrahlung calculations in order to predict the background spectra for charged-particle analysis.[14] These calculations together with the associated X-ray production cross sections have been used to calculate the spectrum for 3 MeV proton excitation shown in Fig. 3. The model assumes the sample form of Fig. 1 with a slight modification due to the reduced range of the protons. An 8 mg/cm^2 substrate is assumed to approximately compensate for the energy loss of the protons in the substrate. The solid line is derived from the theoretical calculations of Ref. 14 whereas the dashed lines are adapted from measurements on very thin substrates.

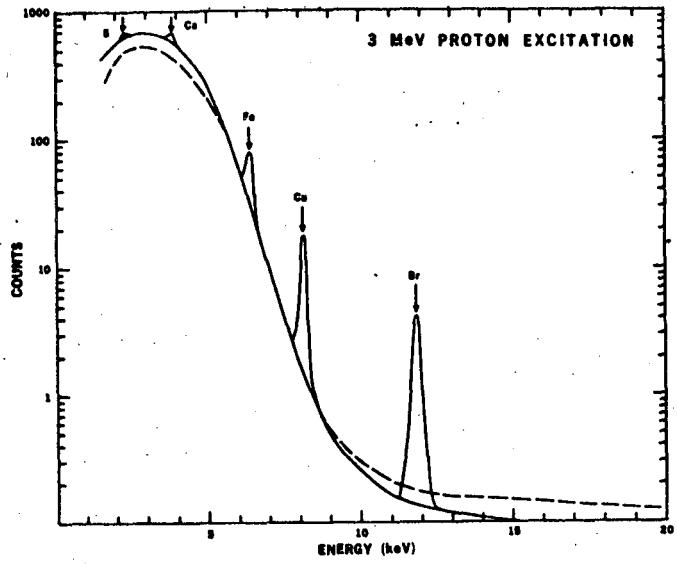

Fig. 3. Calculated spectrum assuming 3 MeV proton excitation. Smooth curve is theoretical background; dashed curve is based on thin film measurements. A 375 μm Be absorber is assumed.

The dominant feature of charged-particle excited spectra is the background intensity at very low energies as indicated in the logarithmic plot of Fig. 3. This is mostly due to secondary-electron Bremsstrahlung. The continuum background due to direct production by the protons would be about three orders of magnitude below the level plotted. The calculated spectrum assumes a low-energy detection efficiency dominated by absorption in a 375 μm Be window. This type of absorption profile has been deliberately chosen to enhance the relative sensitivity for the heavier elements at the expense of the very light ones. A thinner window would enhance the light element sensitivity but the drastic increase in background counts at low energies would reduce the relative counting rate for the higher energy X rays. A compromise solution adopted by some workers is to use a variable attenuation filter consisting of a thick absorber in which a very small hole has been drilled. A normal background reduction is thus maintained over most of the detector area with the exception of a 10% hole through which the low energy spectrum can pass unattenuated.

The theoretical background calculations neglect the effects of electronic pile-up of the low-energy continuum and additional background due to nuclear reactions induced in the sample. These would result in an increased background at the higher energies. On the other hand, a higher peak-to-background ratio is normally achieved in charged-particle analysis through the use of thinner substrates and small area deposits.

Monoenergetic Photon Excitation

The use of photons for fluorescence excitation has the advantage that the radiation is easily available either from radioisotope sources or in conventional X-ray tubes. The fluorescence is induced in the sample by the photoelectric interaction of the incident photons in the inner atomic shells of the elements of interest. An important feature of this interaction is the strong dependence of the cross section on the energy of the incident photon. The maximum value occurs immediately above the binding energy of a particular shell and decreases approximately as E^{-3} as the photon energy is increased. Optimum sensitivity for a given element is therefore achieved using incident energies near the absorption limit.

The background in the spectrum is the result of the elastic and inelastic scattering of the incident radiation in the sample substrate. Elastic scattering results in a change in direction of the scattering photons with no loss in energy. Inelastic scattering causes a loss in energy governed by the kinematic relationship expressed in the Compton equation. For typical X-ray photons, this loss in energy is a few hundred eV or less for each scattering collision.

The simplest case to calculate is monoenergetic photon excitation. This idealized concept is normally approximated in practice by using the characteristic X rays of a particular element as the exciting source. These can be generated either by the direct output from an X-ray source or by a secondary target which is fluoresced by a primary radiation source.

The advantage of monoenergetic or discrete energy photon sources is their ability to optimally excite elements whose absorption edge is slightly lower in energy. Fluorescent peak-to-background ratios can be maximized by confining the scattering of the incident X-ray lines to an energy region of the spectrum where no fluorescent X ray of interest are expected. The disadvantage of the technique results from the loss of sensitivity for those elements whose absorption edges are at a much lower energy. In order to measure these elements efficiently a second fluorescent energy is normally used.

According to the simplified model used in these calculations the spectrum should consist of an elastic scatter peak at the energy of the exciting radiation, an elastic scattering peak at a slightly lower energy, and the fluorescent X rays at their appropriate energies. The area of the scattered peaks is proportional to the appropriate cross section for interaction in the substrate as obtained from the literature.[15] The fluorescent X-ray lines are proportional to the photoelectric cross section in the deposited layers.

Figure 4 shows a calculated spectrum for the case of 17 keV monoenergetic photons incident on the test sample. The dashed line below the inelastic peak represents the background as calculated assuming the simplified model discussed above. The lack of background at lower energies is clearly unrealistic in view of the experimental results. Observed spectra shows a continuous distribution whose intensity is proportional to the high-energy scatter peaks.

Assuming that appropriate measures such as collimation or guard-ring rejection have been used to reduce detector background to a minimum,[3] then it is difficult to attribute the continuous background to any obvious physical processes. Earlier published calculations have estimated the background contributions due to photoelectron induced Bremsstrahlung in the sample and resulting from escape of energetic electrons and their associated Bremsstrahlung from the detector.[16] These effects failed to account for the total observed background.

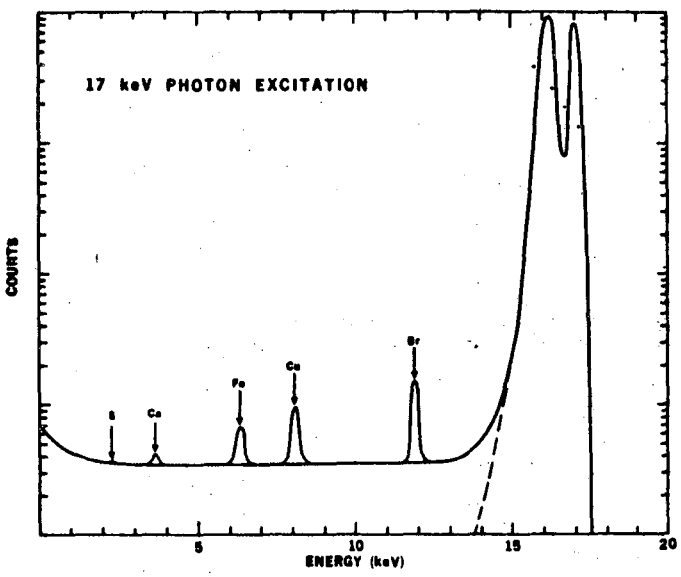

Fig. 4. Calculated spectrum assuming 17 keV photon excitation. The continuous background is based upon a fraction of the total continuous background to scatter peak equal to 2%.

In order to obtain a realistic value for spectral background to use in the calculation, an empirical value for the background level was chosen based on measurements of a low-background guard-ring rejection detector. In the calculated spectrum of Fig. 4 it is assumed that 2% of the scattered intensity is uniformly distributed over the energy range from 0 to 15 keV.

Since the detection sensitivity for the very light elements is greatly reduced due to the energy dependence of the photoelectric cross section, a second measurement is typically performed. Figure 5 shows the calculated spectrums for 4.5 keV photon excitation. It is assumed that 4% of the total scattered intensity is distributed uniformly over the spectrum and that the low-energy X rays are attenuated by a 25 μm Be window. The greatly enhanced sensitivity for Al and S is apparent.

Continuous Photon Excitation

A method for reducing the effects due to the energy dependence of the photoelectric yield is to employ a continuous photon distribution for fluorescence excitation. A continuous distribution guarantees that there will be a portion of the exciting radiation in the energy region most favorable for efficient X-ray production. On the other hand there will also be a portion of the radiation which can be scattered into the region of the spectrum where the fluorescent X rays are to be measured. The net effect is a slower variation of sensitivity with atomic number but with some loss in detectability relative to monoenergetic excitation.

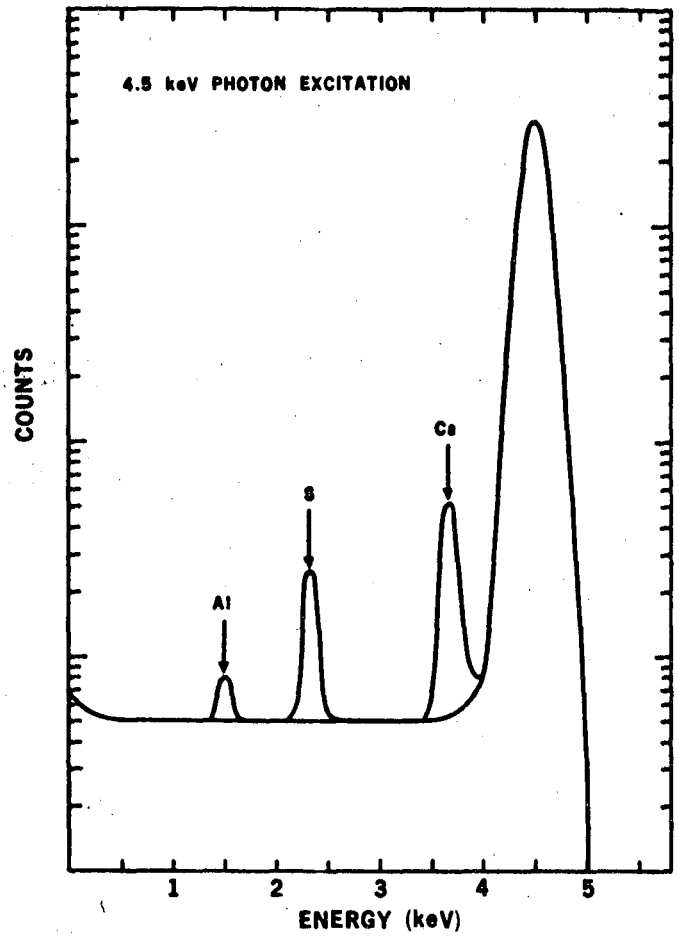

Fig. 5. Calculated spectrum assuming 4.5 keV photon excitation. The background-to-peak ratio is assumed to be 4%.

The present calculations assume a flat energy distribution of incident radiation. The fluorescence intensity is obtained by integrating the photoelectric cross section over this distribution in the region above the K absorption edges of the elements. Two separate cases of background are calculated. A pessimistic estimate is calculated assuming that coherent and incoherent scattering contribute equally to the continuous background. Since at low energies the forward peaked elastic scattering constitutes the major portion of the cross section, it is reasonable to assume that a reasonably designed geometry could reduce this component. A lower limit for the scattered background is calculated assuming that only the incoherent process is present. The actual background would lie somewhere between these two extremes.

Figure 6 shows the calculated spectral responses. A 25 μm Be window is assumed. As expected the peak to background varies more slowly with energy than with discrete excitation. The low-energy background is shown to approach zero at very low energies although in a more realistic calculation the effect of the continuous background due to the detection of high energy events should be included.

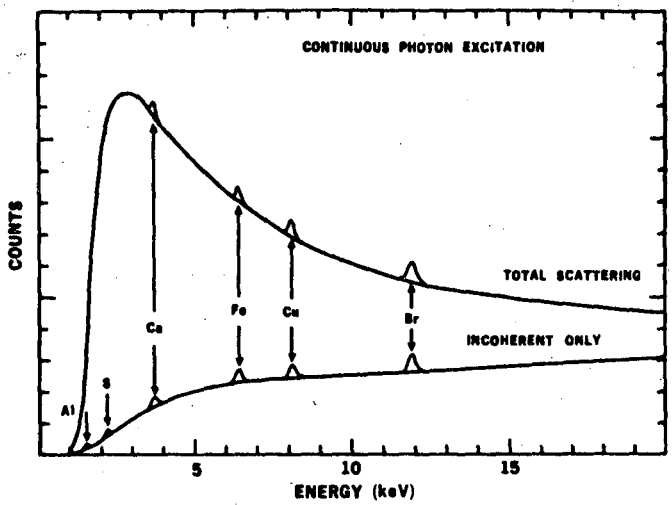

Fig. 6. Calculated spectra assuming a continuous flat photon distribution. The two background spectra represent possible extreme values. More accurate calculations would lie somewhere between these.

COMPARISON OF RESULTS

In order to summarize quantitatively the results of the calculations, the detectable limits for each of the methods have been derived from the model. This limit assumes a value of 3σ where σ is the root mean square deviation equal to the square root of the background under the peak. The comparison is normalized to a total counting rate of 10^4 counts/second for each method consistent with a maximum counting rate limit determined by the pulse processing electronics. The total analysis time is 300 seconds for each.

These conditions are appropriate for high intensity sources such as accelerators or X-ray tubes. The results will probably require scaling to lower counting rates and longer intervals if radioisotope sources are used.

Table 1 is a summary of calculated detectabilities for each of the methods considered. The results appear to agree reasonably well with the trends observed experimentally and in some instances the agreement is better than might be expected on the basis of the simplified calculations. It should be emphasized that these results represent optimistic approximations of what might be achieved under idealized conditions.

The values for Al and S quoted for the 3 MeV protons were calculated assuming a much thinner window (0.025 μm Be) relative to the other elements in the column. A thinner window has the effect of improving the detectabilities for low atomic number elements at the expense of the heavier element values. This follows from the assumption that the counting rate is limited to 10^4 counts/second. Since the low-energy background is such a dominant feature of the spectrum, a large counting rate in this region reduces the relative counting rate at the higher energies. Thus, the absorption of the lower energy portion of the spectrum plays an important role in determining the sensitivity of charged particles.

In the case of photon excitation, the monoenergetic source achieves a better sensitivity in cases where the energies are close to optimal. The detectabilities for continuous excitation exhibit a smoother behavior with energy and are comparable to those for monoenergetic excitation for the very light elements.

TABLE 1

CALCULATED DETECTABILITIES[a)]

	PROTONS 3 MeV	PHOTONS 17 keV	PHOTONS 4.5 keV	CONTINUOUS PHOTONS (Total Scatter)	CONTINUOUS PHOTONS (Incoherent Only)	ELECTRONS 40 keV
Al	.018[b)]		.162	.277	.048	.342
S	.046[b)]	.178	.024	.116	.017	.196
Ca	.018	.062	.010	.068	.015	.164
Fe	.0058	.014		.036	.011	.160
Cu	.0028	.0076		.028	.010	.195
Br	.014	.0038		.021	.009	.277

a) Expressed as μg/cm² referred to a 25 mg/cm² substrate. Results are based upon simplified theoretical models described in the text assuming 10^4 cts/sec and 300 sec intervals.

b) Results for Al and S were calculated assuming a 25 μm Be window. The remaining elements were calculated assuming 375 μm Be.

Although one is tempted to pursue these comparisons into greater detail, it is probably best to limit the discussion to these few observations in view of the approximate nature of the calculations. However, the calculations do give one the assurance that the models represent a reasonable interpretation of the actual processes involved in each excitation method. In all but the case of monoenergetic excitation, the calculations are based upon fundamental physical interactions inherent in the irradiation process. For monoenergetic excitation, a semiempirical approach was required to quantify the effect of continuous spectral background.

TECHNIQUES FOR IMPROVEMENT

Some improvement in the capabilities of each method relative to the calculated values is possible. The use of thinner substrates and variable attenuation absorbers have already been discussed with reference to charged-particle excitation.

The detectability of photon excited analysis could be improved if the magnitude of the scattered radiation could be reduced. Several authors have attempted to employ linearily polarized photons for excitation in order to take advantage of the minimum scattering in the direction of the polarization.[17-19] Although a relative reduction in background to fluorescence signal has been observed, it has not proved practical to construct high intensity polarized sources by conventional techniques.

All of the methods can profit by the ability to handle higher counting rates in the pulse processing system. The technique of pulsed excitation has been employed successfully in each case with the accompanying increase in output counting rate.[20-22] The method of pulsed excitation also has a number of secondary advantages such as the reduced target heating which benefits charged-particle techniques.

The question of the continuous background induced by the high-energy scattered photons is an important area for improvement in the case of monoenergetic excitation. Insofar as this effect cannot be attributed at present to any fundamental interactions involved in the irradiation and detection processes, it is hoped that future developments might reduce this background contribution considerably.

CONCLUSION

The observed energy dispersive X-ray fluorescence spectra obtained with various forms of fluorescence excitation can be described using simplified physical models. Theoretical and semiempirical calculations based on these models give reasonable agreement with experimental values for sensitivity and detectability.

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