DETECTOR BACKGROUND AND SENSITIVITY OF X-RAY FLUORESCENCE SPECTROMETERS

Goulding, F.S.

1971-05-01

To be submitted to Advances in
X-ray Analysis, Vol. 15;
20th Annual Denver X-Ray Conference,
Denver, Colorado, August 11-13, 1971

LBL-9
Preprint c.2

DETECTOR BACKGROUND AND SENSITIVITY OF X-RAY FLUORESCENCE SPECTROMETERS

F. S. Goulding, J. M. Jaklevic, B. V. Jarrett,
and D. A. Landis

July 16, 1971

AEC Contract No. W-7405-eng-48

DETECTOR BACKGROUND AND SENSITIVITY OF X-RAY FLUORESCENCE SPECTROMETERS

F. S. Goulding, J. M. Jaklevic,
B. V. Jarrett and D. A. Landis

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

ABSTRACT

Degraded detector pulses are shown to contribute most of the background in spectra produced by semiconductor-detector X-ray spectrometers. A new guard-ring detector is used with appropriate circuits to reduce background by a large factor. We discuss the sensitivity of the new arrangement with various excitation sources.

INTRODUCTION

Semiconductor-detector X-ray fluorescence spectrometers are now commonly used for analysis of materials for constituents present at levels over 10 ppm. Slightly lower limits of detection can be achieved in favorable circumstances, and if long counting times are employed. However, the sensitivity range below 1 ppm, which is of great interest in biological and environmental studies, is not easily accessible using existing X-ray spectrometers--the purpose of the work described here is to lower detection levels down to about 0.1 ppm.

In the past, work on semiconductor-detector spectrometers has been primarily aimed toward improving energy resolution. This was an essential step in order to achieve separation of peaks due to adjacent elements; furthermore, reduction of the width of peaks improves the peak-to-background ratio, thereby lowering the limit of detectability for trace elements. It is important to realize, however, that reducing background achieves the latter objective too, and this is the course pursued in the present work.

Figure 1 shows the X-ray spectrum produced by a conventional spectrometer using molybdenum X-ray excitation of a blood serum sample. The exciting radiation was derived from a molybdenum fluorescer excited by an ^{125}I ring source. In a system of this type, no low-energy radiation is produced by the exciting source, and the semiconductor detector should observe only fluorescent X-rays from the sample together with the exciting radiation backscattered by the sample. In practice, well over 90% of the counts should occur in the backscatter peak at the high-energy end of the spectrum, but, if degraded in any way, they constitute a general background hiding the peaks characteristic of trace elements in the specimen. In the case shown in Fig. 1, about 20% of the backscatter events are degraded to produce background.

We shall show that these degraded background pulses are the result of imperfect charge collection in detectors, and that they can be virtually eliminated by new detector techniques.

DETECTORS IN X-RAY SPECTROMETERS

Figure 2 shows three silicon detector configurations used in X-ray spectrometers. The first type, originally used by Miller (1) is referred to as the "top-hat" geometry, and is characterized by low-leakage current and excellent high-voltage behaviour. Both characteristics are desirable in high-resolution spectrometers, so this configuration is commonly used in these applications. The second type, the "grooved" detector, was used originally by E. Woo, and now employed in "Kevex" X-ray systems, possesses the same advantages as the "top-hat" geometry. The third geometry, generally referred to as "planar", exhibits higher leakage current and capacity than the other two types, and is therefore rarely used in X-ray spectrometers. However, its background properties probably deserve investigation. Llacer (2) analyzed the behaviour of these geometries with regard to their ability to sustain high-voltage operation, and to produce low leakage current. His results, and those obtained in our laboratory, indicate that an n-type surface channel normally exists on the surface of silicon detectors. This channel acts as an extension of the n-type lithium-diffused region, and since it represents a poor junction to the bulk material, it contributes most of the leakage current, and sets the voltage limitation on detector operation . The fact that such channels can be "pinched-off" by internal electric fields normal to the surface explains the difference in behaviour between the structures of Fig. 2a and 2b and that of Fig. 2c.

These arguments fail to take into account the collection of charge produced by radiation in the bulk of the detector. The presence of n-type surface layers distorts the internal electric field pattern in the detector in such a way that collection of charge produced by X-rays interacting in some parts (shown by horizontal-line-shading in Fig. 2) is via the surface layers. This causes a loss of charge, so that signals that should appear in the backscatter peaks appear in the general background in spectra. The tests presented in this paper show that this is the predominant source of background in existing spectrometers.

At first sight it may appear that collimation of X-rays to prevent their interaction in the poor field regions might reduce background, and, indeed, tests show that some improvement can be achieved by this method. It is also obvious that improvement results from increasing the detector area while collimating to a small central region, but the large consequent increase in detector capacity seriously degrades the system resolution--an intolerable price to pay. The degree of collimation that can be used is determined by the requirement for good sample-detector geometry; as shown in the typical geometry shown in Fig. 3, this implies a wide divergence of X-rays hitting the detector. Despite the possible auxiliary collimator shown in this figure, mounted on the detector face--an expedient rarely adopted as it is difficult to change this collimator to suit the energy range of interest--X-rays like that travelling from A to B still interact in regions of poor charge collection. On the other hand, the X-ray from C to D interacts in a region of good charge collection, and produces the correct signal.

As shown in Fig. 4, the background due to degraded pulses increases as the energy of the X-rays impinging on the detector increases. For cadmium X-rays, the total integrated background count approaches the total number of counts in the main X-ray peak. The proportion of counts in the background decreases considerably in the case of zirconium, and still further for lower energy X-rays.

THE GUARD-RING DETECTOR METHOD

Guard rings have been employed for many years to overcome fringing field effects in standard capacitors, and have also found application (3) in semiconductor detectors as a device to reduce edge leakage. It therefore seems an obvious step to use a guard ring to define the boundary of the sensitive volume of a detector by internal electric field lines rather than by a physical surface with its unknown charge-trapping characteristics. This can also be considered as an electronic collimation technique. Figure 5a shows the simple implementation of the idea; note that the output signal is derived only from the central region, while the guard ring and the central region are maintained at the some dc potential (ground).

Even this configuration suffers from a signal degradation problem at the edge of the central region. The initial X-ray interaction in this peripheral region produces a dense cloud of charge ~ 5 microns in diameter; in the electric field, holes and electrons are separated, drifting toward their appropriate electrode. The internal repulsive fields existing within the hole and electron clouds are very large compared with the drift field in the detector--therefore, the cloud dimensions rapidly increase until the internal repulsive field approaches the same value as the drift field. This means that the cloud dimensions reach about 100 microns during the charge collection process. Consequently, a peripheral region of 100 microns thickness exists around the sensitive region from which only part of the charge due to an event is collected in the central region--this means that many of the backscattered events appear in general background. Our measurements show that the background present with a simple guard-ring detector is from 2 to 10 times smaller than that with a top-hat detector, the exact factor depending on the energy of the backscatter peak.

A further reduction in background is achieved by sensing coincident signals between the guard-ring and central regions, and rejecting the central region signal when such a coincidence is registered. This "guard-ring reject" system effectively eliminates the partial collection from the peripheral region of the sensitive volume of the detector. With such an arrangement, we approach the background level expected due to electron escape from the detector surface. In our actual detector, shown in Fig. 5b, a double guard-ring is used, the outer ring serving to reduce edge leakage in the inner ring, and thereby improving its noise properties so that the inner guard-ring signal discriminator can be set low to detect very small signals.

The improvement in background resulting from use of the guard-ring reject method is shown in Fig. 6. Using exactly the same geometry, cadmium X-rays scattered from lucite were used to irradiate a standard top-hat detector (a), and the guard ring reject detector system (b). For the same number in the cadmium peak, total counts recorded in the background is 40 times smaller for the guard-ring reject system than for the top-hat detector. Larger factors are obtained when the detectors are irradiated by radiation of higher energy than cadmium X-rays.

Figure 7 illustrates the improvement achieved by using this technique on a typical sample. The same blood serum sample used for Fig. 1 was examined, and the same total number of counts was accumulated in the molybdenum X-ray backscatter peak. The reduction in background seen in this spectrum, averaged over the full energy range, is about a factor of 15. Much larger factors, ranging up to about 60, have been observed for higher-energy excitation. Comparison of Fig. 7 with Fig. 1 shows the improvement in ability to see small traces of elements, such as nickel, present in the specimen at a level near 0.1 ppm. Better statistics realized by a longer count, or with more intense excitation, would further reduce the detection limit.

CALCULATION OF SENSITIVITY LIMIT

It is interesting to calculate the detection limit for an X-ray fluorescence spectrometer, and to relate this to detector background. We will consider the case of traces of lead in an organic matrix, using molybdenum Kα excitation, and will assume that only the lead Lα peak is used for the analysis.

We have:

Total scattering cross-section for molybdenum Kα radiation in an organic matrix = 5 barns/atom.

Total L-shell photoelectric cross-section for lead = 3×10^4 barns/atom.

Fluorescent yield for lead L X-rays = 0.4

Fraction of L X-rays in Lα peak $\simeq 0.5$

$\therefore$ Effective cross-section for lead Lα production $\simeq 6 \times 10^3$ barns/atom.

Now

$$\frac{\text{No of lead atoms}}{\text{No of matrix atoms}} = \frac{0.06\,P}{10^6}$$

where P is the lead concentration in ppm by weight.

$$\therefore \frac{\text{No of Pb L}\alpha\text{'s at detector}}{\text{No of scattered X-rays at detector}} = \frac{6 \times 10^3}{5} \cdot \frac{0.06P}{10^6}$$

$$= 7.2P \times 10^{-5} \qquad (1)$$

Now assume that N counts are accumulated in the backscatter, and that X% of these appear in a flat background from zero amplitude to the amplitude corresponding to the backscatter energy. Recognizing that the width of fluorescent lines is about 1% of the backscatter energy we find:

$$\text{No of background counts beneath lead L}\alpha\text{ peak} = \frac{N.X}{10^4}$$

Experiment shows that a reasonable detection limit for the counts in a peak is twice the R.M.S. deviation in the background under the peak.

$$\therefore \text{Detectable limit} = 2 \times 10^{-2} \cdot \sqrt{N.X}\ \text{counts} \qquad (2)$$

But Eq. 1 shows that the number of counts in the lead Lα peak is equal to 7.2 P.N. 10^{-5}.

$$\therefore \text{Detection limit, expressed in ppm by weight} = P_{LIM}$$

$$= 300\sqrt{\frac{X}{N}}\ \text{ppm} \qquad (3)$$

Typically the value of N might be 10^6, and we might assume $X = 20$ for a top-hat detector, while $X = 1$ for a guard-ring reject system.

$\therefore P_{LIM}$ for top-hat detector $\simeq 1.3$ ppm.

and P_{LIM} for G-R system $\simeq 0.3$ ppm

Using a monochromatic X-ray tube (4), counts can be accumulated at a rate of 2×10^4 per second, limited by the counting rate capability of the pulsed-light feedback electronics we use. This means that the sensitivities we have derived are achieved in only 50 second counts. If the counting time is increased to ten minutes, a limit of detection of 0.1 ppm is comfortably achieved.

CONCLUSION

The guard-ring detector technique described here reduces background in X-ray fluorescence spectrometers by a large factor, the improvement increasing with higher exciting energies. The sensitivities that can be achieved using this technique, together with a monochromatic X-ray tube, extend the use of X-ray fluorescence spectrometers into the range of biological trace elements (5). The resulting instrument provides the capability of rapid analysis for a broad range of trace elements with only very simple sample preparation.

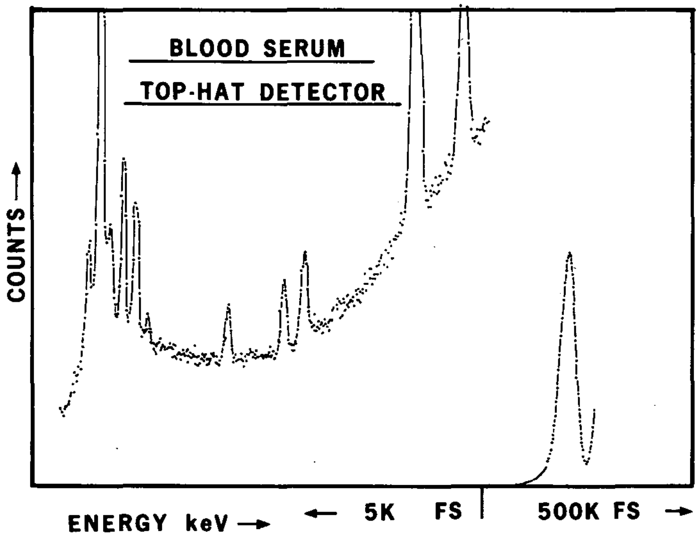
ACKNOWLEDGMENTS

We thank J. Walton and H. Sommer for their making the detectors used in this investigation, and R. Giauque for advice on analytical aspects of the problem.

This work was carried out as part of the program of the Nuclear Chemistry Division of the Lawrence Berkeley Laboratory under the United States Atomic Energy Commission Contract No. W-7405-eng-48.

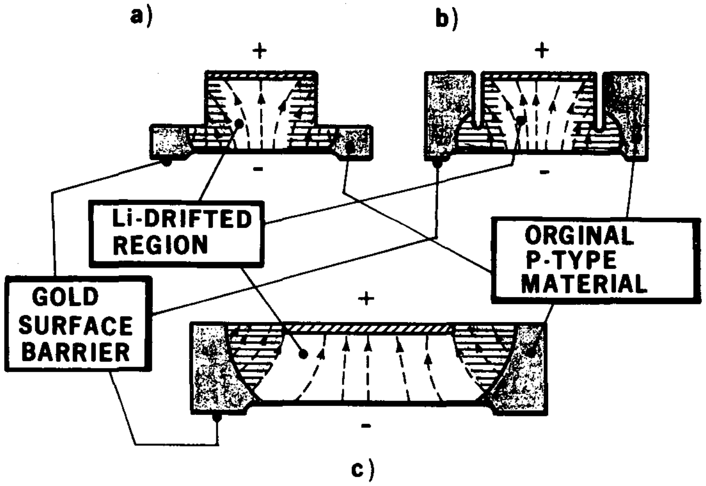
REFERENCES

1. G. L. Miller, private communication referenced in Llacer's paper (Ref. 2) p. 99.
2. J. Llacer, "Geometric Control of Surface Leakage Current and Noise in Lithium Drifted Silicon Radiation Detectors", IEEE Trans. Nucl. Sci. NS-13, No. 1, p. 93 (1966).
3. W. Hansen and F. S. Goulding, "Leakage, Noise, Guard Rings and Resolution in Detectors", Proceedings of Asheville Conference NAS-NRC Report No. 32, 202 (1961).
4. J. M. Jaklevic, R. D. Giauque, D. F. Malone and W. L. Searles, "Small X-Ray Tubes for Energy Dispersive Analysis Using Semiconductor Spectrometers", Lawrence Berkeley Laboratory Report No. LBL-10. Presented at the 20th Annual Denver X-ray Conference Aug. 11-13, 1971.
5. F. S. Goulding and J. M. Jaklevic, "Trace Element Analysis by X-ray Fluorescence", Lawrence Radiation Laboratory Report No. UCRL-20625, Berkeley, California.



XBL 717-1177

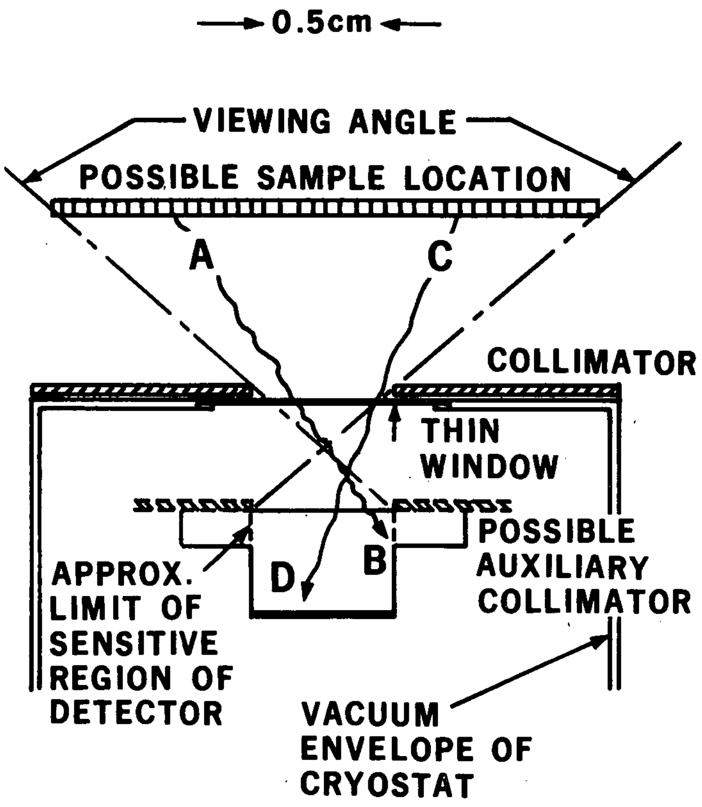
Figure 1. Fluorescence X-ray spectrum of a blood serum specimen using a conventional silicon detector spectrometer.



XBL 717-1179

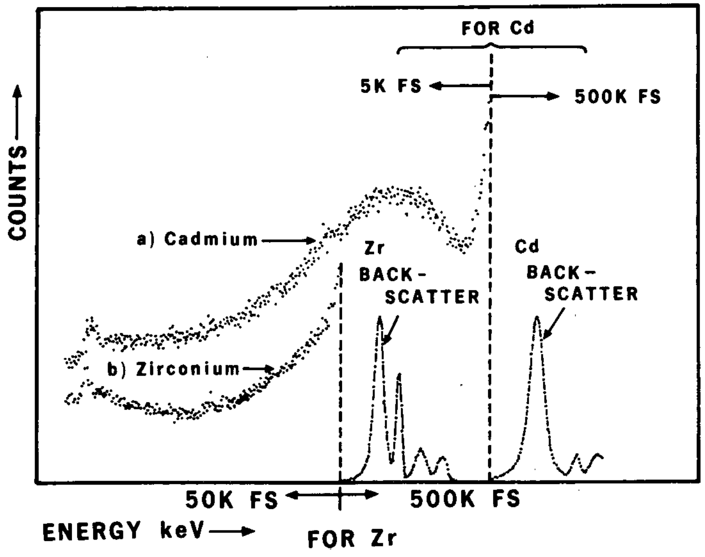
Figure 2. Types of detector configuration used in X-ray spectrometers:

a) Top-hat detector
b) Grooved detector
c) Planar detector



XBL 717-1175

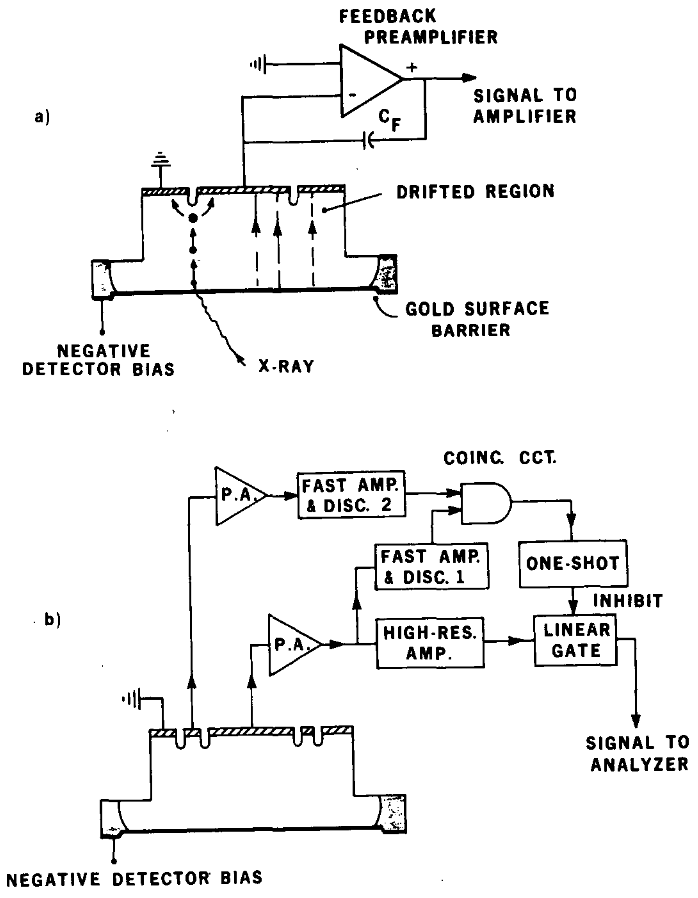
Figure 3. Preferred collimation geometry for an X-ray spectrometer.



XBL 717-1176

Figure 4. Showing the variation in background of a top-hat detector as a function of the energy of radiation striking the detector.

a) Cd X-rays scattered by lucite.
b) Zr X-rays scattered by lucite.

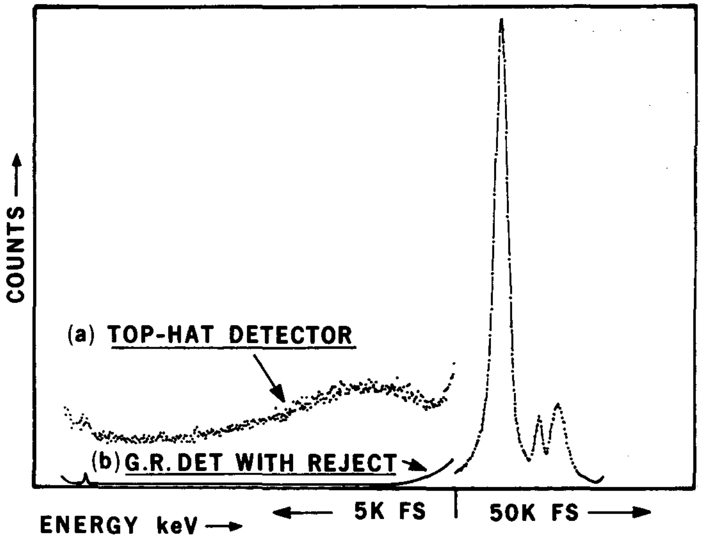


XBL 717-1181

Figure 5. Guard-ring detectors.

a) Simple guard-ring approach showing the mechanism for degraded pulses.

b) Double guard-ring detector with pulse-reject circuitry to remove degraded pulses.

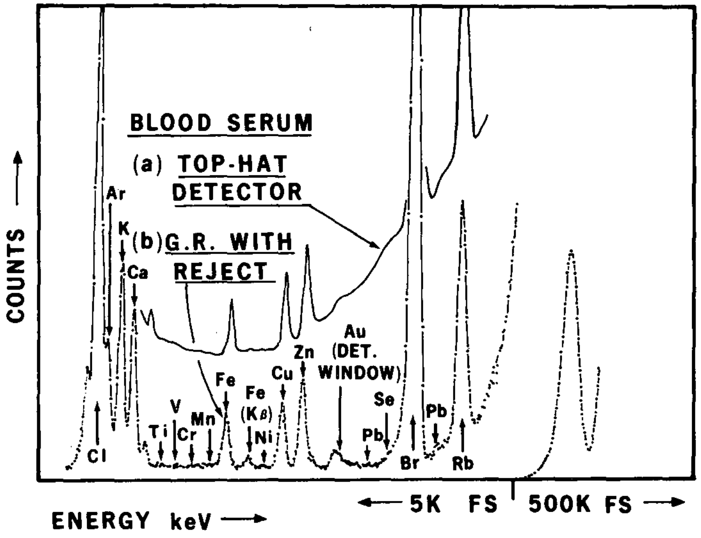


XBL 717-1178

Figure 6. Background produced in detector systems by Cd X-rays.

a) Top-hat detector.

b) Guard-ring detector with reject circuitry.



XBL 717-1180

Figure 7. Fluorescence X-ray spectrum obtained on a blood serum specimen using a spectrometer equipped with guard-ring detector and reject circuitry (b). For comparison, the spectrum obtained on the same sample with the same geometry, and the same total counts in the scatter peak, but with a simple top-hat detector, is also shown (a). This is a smooth curve drawn through the points of Fig. 1.

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720