

Reports

Application of High-Resolution Semiconductor Detectors in X-ray Emission Spectrography

Abstract. Solid-state devices developed primarily for nuclear gamma spectroscopy have many potential uses in x-ray analysis.

Solid-state devices for the detection and energy measurement of nuclear γ -radiations have been greatly improved in the past 3 years (1). In particular, semiconductor diodes of silicon and germanium and the electronic circuitry required for their use have improved so greatly that existing detectors can absorb electromagnetic radiation with efficiency approaching 100 percent and deliver output pulses directly proportional to the energy of individual photons. The energy discrimination achieved in apparatus functioning in our laboratory (2) is good enough to permit one to distinguish photons differing in energy by as little as 1.1 kev. This resolving power can be maintained at very high counting rates. This energy discrimination makes it possible to measure and distinguish the characteristic x-rays of various chemical elements, even elements differing by only one unit in atomic number.

These solid-state devices have very attractive applications in the rapid, non-destructive chemical analysis of materials. In particular, an extremely compact, convenient, and rapidly functioning system can be assembled from a radioactive source of moderate strength, a sample-holder, and a semiconductor photon-counter, plus electronic circuits for linear-pulse amplification and pulse-height analysis of the output signal from the detector. The radioactive isotope serves as a source of primary radiation to excite characteristic x-rays of the elements in an analytical sample. The semiconductor device and its associated circuitry measure the number and energy of the secondary x-rays.

Such a system does not have as great energy-resolving power as that

achieved in commercial x-ray emission spectrometers. Nonetheless, the greater simplicity of the semiconductor system and a number of other favorable features would make it an extremely useful substitute or even an improvement in many applications.

The fundamental principles of semiconductor counter for nuclear spectroscopy, as well as recent improvements, both in device manufacture and in associated electronic circuitry, are described elsewhere (1). We do not deal with these matters here except for a few comments on photoelectric efficiency, presented immediately below, and the details of our own detectors, which we present later in the report. Performance with respect to energy resolution will be apparent in our experimental results.

Later in this report we describe experiments which demonstrate not only the excellent performance of the detectors for x-ray analysis but also the feasibility of their use in an x-ray emission spectrograph.

Aside from good energy resolution, the attractiveness of the semiconductor detectors stems from their high efficiency for conversion of incident photons into electrical output pulses. We consider only silicon and germanium, as these are the only materials at the present stage of technology which are readily available for use in radiation detectors. Also, in practice we shall limit ourselves to detectors doped with lithium. Silicon detectors are widely used also as particle detectors (protons, alpha particles, and so forth), but we shall refer in this report only to their use in the detection of photons.

Photons are absorbed in silicon or

germanium by the photoelectric effect, by Compton scattering from electrons, or, in the case of high-energy photons, by creation of electron positron pairs. The probability of these processes is a strong function of the photon energy and of the atomic number of the absorbing material. Figure 1 illustrates these probabilities as a function of energy for silicon and germanium in detectors of 3-mm sensitive depth. We can dismiss pair production as of no significance for our purposes because the threshold energy of 1.022 Mev lies manyfold higher than the x-ray energy of the heaviest elements. The Compton process has a high probability, but, in general, Compton scattering is not useful in energy analysis because it causes incomplete and variable deposition of energy in the counter; hence, it contributes to the background over a wide energy region. The principal useful effect is photoabsorption, because the entire energy of the photon is released in the detector and a "line" is obtained in the energy spectrum. In a detector with a sensitive layer several millimeters thick, there is a substantial contribution to the line spectrum by multiple processes—that is, by photoabsorption of scattered gamma rays. Contributions of such multiple processes to the photopeak are included in the computations upon which Fig. 1 is based.

Inspection of the curves for the photoelectric effect shows that silicon is most useful for low-energy γ -ray photons. At 30 kev the absorption probability is still about 50 percent. Hence, silicon diodes 3 mm thick can serve as good detectors of K x-radiation for elements up to barium (element 56) or somewhat higher. The use of silicon has the further effect that it de-emphasizes the contribution of K x-radiation of higher elements because the photoelectric absorption drops off so steeply. Hence it is the material of choice for study of K x-rays of the lighter elements. It is also useful for the measurement of L x-rays of the heavier elements.

There is a lower energy cutoff set by absorption of photons in the radiating sample and in the counter window and by various sources of noise in the detector and the associated amplifiers. In the data presented here this limit is about 4 kev, so that x-rays of elements below about scandium (element 21) cannot be clearly resolved. Future advances may reduce this limit somewhat.

Germanium is the favored counter

material for the heavier elements (K x-ray energies up to 120 keV). Figure 1 indicates a 50-percent photopeak efficiency at 100 keV. It should be noted that this is for a sensitive layer 3 mm thick, a thickness which is obtained routinely by present technology in many research laboratories and commercial laboratories. Working detectors of several times this thickness have been made, and one can anticipate that such devices will be generally available in the near future.

Hence, by proper choice of silicon or germanium, one can select a detector with 50- to 100-percent efficiency over the whole range of energies of interest to x-ray emission spectroscopy. This efficiency is, of course, for radiation actually reaching the detector. The finite size of the detectors, typically 1 to 10 cm² in cross section, and the necessity to position the sample some centimeters away will introduce a geometry factor which will decrease the overall efficiency.

We performed a series of experiments with our apparatus arranged as in the schematic drawing, Fig. 2. Radioactive sources of ²⁴¹Am or ⁵⁷Co were placed near a semiconductor detector of silicon or germanium. The detector was heavily shielded from this radioactivity. Various materials, principally pure metallic foils, were placed in such a position that the radiations of ²⁴¹Am or ⁵⁷Co could reach the sample and excite therein the characteristic x-rays. The x-radiation was in direct view of the detector. Electrical pulses from the detector were amplified and subjected to pulse-height analysis. Important details of the component parts of our apparatus are given in the following paragraphs.

Americium-241 is an excellent source of primary radiation for the excitation of characteristic x-rays of the elements, particularly those with lower atomic numbers. Table 1 lists some pertinent details of its radiations. Figure 3 shows the spectrum of γ -rays and x-rays emitted by ²⁴¹Am. It is an alpha- and gamma-emitter with a half-life of 470 years, available in an isotopically pure form from plutonium samples containing the isotope ²⁴¹Pu. It provides constant activity at high specific activity. The alpha radiation is easily screened out with a few milligrams of absorber per square centimeter. The 59.57-keV γ -ray which it emits in 40 percent of its disintegrations has a convenient energy for absorption in the K-electron

shell of elements up to erbium (element 68) and in the L-electron shell of heavier elements.

Lead can be used to collimate the ²⁴¹Am radiation and to shield it from the detector without danger of exciting lead K radiation in the collimator. Americium also emits L x-rays of neptunium in an intensity of about 20 percent (see Table 1). These x-rays are quite effective in exciting the K radiation of elements up to yttrium (element 39).

Hence, the combination of ²⁴¹Am for primary radiation and a silicon detector for analysis of secondary radiation is very favorable for efficient excitation and detection of K radiation of elements up to the lighter rare earths and for strong discrimination against excitation of K x-radiation of elements of higher atomic number.

In our experiments we used a source strength of approximately 10⁸ disintegrations per minute, encapsulated in a thin plastic button and placed immediately below the housing of the semiconductor detector. A lead foil 20 mm thick was placed around the sample housing to shield the detector from the ²⁴¹Am radiations.

For excitation of K x-radiation of heavy elements we used a ⁵⁷Co source. Cobalt-57 has a half-life of 267 days, decaying by orbital electron capture. It emits prominent γ -rays of 122- and 136-keV energy (see Table 1).

Our ⁵⁷Co source, which had a strength of approximately 2×10^9 disintegrations per minute, was placed in a 1-cm hole drilled in a lead block. The lead thickness between the sample and the detector was 2.5 cm, or approximately ten half-thicknesses for absorption of the 136-keV radiation. A background problem arose because of the excitation of lead K x-rays in the absorber. This background was greatly reduced by lining the hole and top surface of the lead block with thin layers of cadmium and copper.

Our lithium-drifted germanium detector was a LRL-Livermore-type diode (3) with dimensions of $3 \times 1 \times 0.3$ cm and capacitance of 1.9 pf (2). The detector bias (-2000 volts) was applied to the front face of the detector after passing through a filter network having a time constant of 10 seconds. The long time constant protected the n-channel field effect transistor (FET) from damage resulting from transients created in turning the bias supply on or off. The detector and the FET

Table 1. Characteristics of γ - and x-radiations emitted by ²⁴¹Am (half-life 470 years) and ⁵⁷Co (half-life 267 days).

| Nuclide | Energy of radiation (keV) | Intensity per disintegration |
|-------------------|-----------------------------|------------------------------|
| ²⁴¹ Am | 59.57 | 0.36 |
| | 26.36 | .025 |
| | 13.96 L α_1 Np x-ray | .12 |
| | 17.76 L β_1 Np x-ray | .13 |
| | 20.80 L γ_1 Np x-ray | .03 |
| ⁵⁷ Co | 122. | .9 |
| | 137. | .1 |

(2N3823) were mounted in a vacuum chamber and operated at the temperature of liquid nitrogen. The detector was electrically insulated from ground potential by means of a sapphire rod which also served as a heat conductor. A very thin beryllium window (0.02 cm) was used as the front wall of the chamber containing the counter.

The lithium-drifted silicon detector was a LRL-Berkeley-type diode (4) 1.4 cm in diameter with a 2.5-mm-deep sensitive layer. It had a capacitance of ~ 3 pf. A highly filtered detector bias voltage of -240 volts was applied to the front face (anode) of the detector. The silicon detector was operated at $\sim -100^\circ\text{C}$ and the FET(2N3823) operated at liquid-nitrogen temperature. Ceramic insulators were used to provide electrical isolation. The temperature of the detector was adjusted by using a large diameter bias voltage wire (No. 6) which served to conduct external heat to the detector. In other respects the experimental arrangement was the same as that described for the germanium detector above.

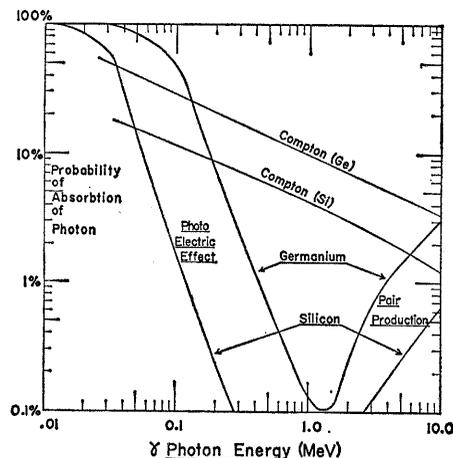


Fig. 1. Probability of absorption of γ -ray photons in silicon and germanium detectors 0.3 cm thick. [Figure prepared by F. Goulding]

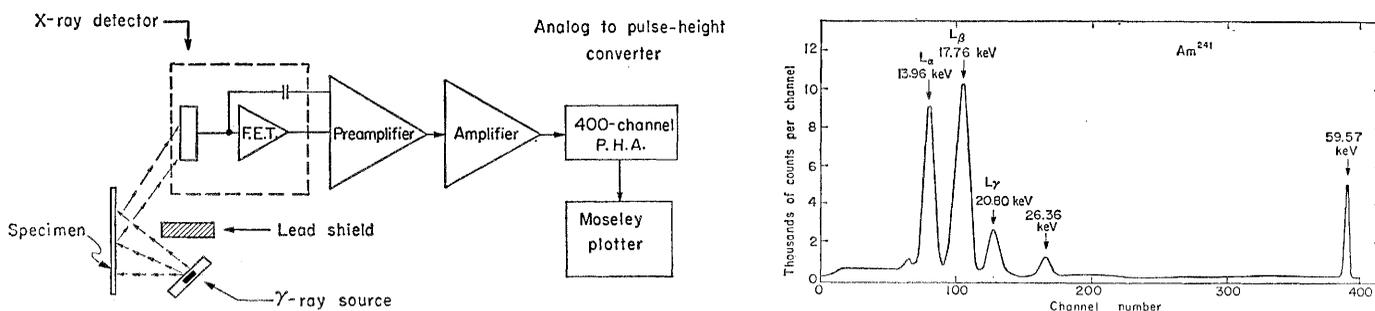


Fig. 2 (left). Schematic arrangement of apparatus for excitation and measurement of characteristic x-radiation of an analytical sample. That part of the apparatus outlined in dashed lines is maintained at low temperature. Fig. 3 (right). Gamma and x-radiation emitted by ^{241}Am . This spectrum taken by a silicon semiconductor detector. Americium-241 shielded only by a 2-mm-thick plastic cover which absorbed alpha particles.

The FET preamplifier was mounted in the vacuum chamber and served as the first stage of a charge-sensitive preamplifier. The rest of the preamplifier was mounted outside of the chamber with the feedback line returning to the input of the FET through a 1-pf porcelain condenser. The same preamplifier was used both for the germanium and for silicon detectors. This preamplifier is essentially the one described by Elad (2).

A number of commercial amplifiers were tested to determine their contribution to the overall resolution of the system. In the case of the lithium-drifted germanium detector, the resolution appeared to be independent of the main amplifiers as tested under conditions of slow counting rates. In the case of the silicon detector, noticeable improvement in the system resolution was obtained by using the Tennelec (model TC 200) amplifier for low counting rates. At very high counting rates the Tennelec amplifier gave the best resolution for both detector systems.

The pulse-height analyzer used for the measurement was a standard 400-channel RIDL analyzer which included provision for operation in the conventional add-and-subtract mode. This made it possible to subtract the background automatically. Three different commercial pulse-height analyzers were used to measure the energy resolution of the system and to determine whether one type would have advantages over the others. All three types of analyzers, namely, RIDL, TMC, and Nuclear Data, gave the same resolution, as determined with a 122-keV γ -ray line from ^{57}Co . The x-ray energy distributions were plotted with a Moseley-type x - y plotter.

In each experiment with the silicon detector, a pure metallic foil with thick-

ness 0.002 to 0.02 cm was placed about 5 cm away from the detector, in such a position that the radiations of ^{241}Am could irradiate the foil. The counter was operated for a 2-minute period, after which the metallic foil was removed and the detector was operated for an additional 2-minute period with the multichannel analyzer set in subtract mode. Gram-sized samples of rare-earth oxides were placed in thin-walled cellulose nitrate tubes and studied in a similar way. Results of all experiments

are shown in Fig. 4. These experiments were run in succession under conditions of good stability in the overall system. No change in amplifier gain settings was made between runs, so that the energy scale is the same throughout. Also, the count scale is the same in all spectra, but the zero level has been adjusted in the figure for clearer presentation of the data.

In the group of elements titanium through copper, there is no separation of the components of the K radiation,

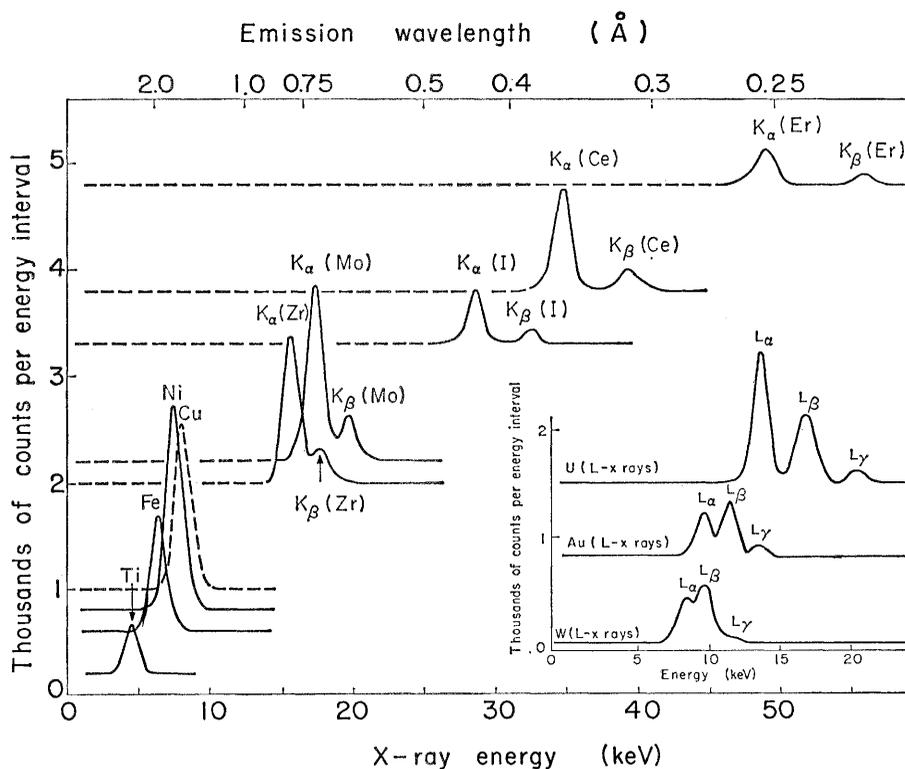


Fig. 4. K x-ray spectra of several elements taken with lithium-drifted silicon detector. Americium-241 source was used to excite characteristic x-rays. Each spectrum represents a separate experiment with a metallic or oxide sample of the element. Counting period was 2 minutes. Vertical scale is linear in the number of counts but the zero of the scale lies at a different level for each element. Energy values in the figure are taken from tables. Integrated count in K x-ray peak is given in Table 2. The inset shows L x-radiation excited in heavy elements by ^{241}Am radiation. Data collection for 2-minute period. Vertical scale identical to main figure.

but there is a definite shift in the location of the x-ray peak. The x-rays of titanium lie close to the lower energy limit set by the electronic noise in the system. For zirconium and heavier elements, the $K\alpha$ and $K\beta$ groups are separated. Erbium (element 68) is the heaviest element whose K x-rays can be excited by the 59.57-keV γ -radiation of ^{241}Am . Representative spectra of L radiation of tungsten, gold, and uranium are shown in the inset in Fig. 4. Our energy resolution expressed in units of full width at half maximum is 1.3 keV, or 9.5 Å, for nickel x-rays, and 1.2 keV, or 10.3 Å, for cerium x-rays.

Table 2 lists the target elements used in the experiments, together with the accurate values of x-ray energies taken from published tables (5). Table 2 also lists the total count recorded in the x-ray peak for each element. These numbers provide only a rough indication of sensitivity, because sample size and placement were not precisely measured or reproduced.

Figure 5 shows spectra taken on solutions of silver nitrate held in thin-walled cellulose nitrate tubes. The lower curve is for a 5-ml solution containing 0.5 g of silver. The analysis time was 2 minutes. The upper curve is for 10 mg of silver in 1 ml of water, with a counting period of 7 minutes. In another experiment, 10 mg of zirconium in 2 ml of solution were identified. Owing to elastic scattering of the primary radiation by the solution, the background is higher than in the case of metallic samples. Correction for this background was made by running with blank samples of pure water in the sample position. Figure 6 shows spectra taken on samples of solder (60 percent Pb and 40 percent Sn) and phosphor bronze to indicate the usefulness of the technique for the quick identification of common materials.

For the experiments with the lithium-drifted germanium detector a ^{57}Co source was used for the primary radiation. The material to be analyzed was placed in front of the detector, where it was directly illuminated by the ^{57}Co γ -radiations.

In the first set of experiments, foils of tantalum, platinum, gold, lead, thorium, and uranium were placed in the sample position. Data were collected for 2 minutes. Settings of gain controls on the amplifiers were the same throughout the series, but the pulse-height threshold control on the 400-channel pulse-height analyzer was ad-

Table 2. Characteristics of samples used in fluorescence experiments with silicon semiconductor (see Fig. 4).

| Element | Atomic number | X-ray energies (in keV) | | | | Sample used in experiments | Total counts in K peaks in 2-min run |
|---------|---------------|-------------------------|-------------|------------|------------|---------------------------------|--------------------------------------|
| | | $K\alpha_2$ | $K\alpha_1$ | $K\beta_1$ | $K\beta_2$ | | |
| Ti | 22 | 4.51 | 4.50 | 4.93 | | 50- μ metal foil | 3,800 |
| V | 23 | 4.94 | 4.95 | 5.43 | | 100- μ metal foil | 2,200 |
| Fe | 26 | 6.39 | 6.40 | 7.06 | | 150- μ metal foil | 9,300 |
| Ni | 28 | 7.46 | 7.48 | 8.26 | | 500- μ metal foil | 18,000 |
| Cu | 29 | 8.03 | 8.05 | 8.90 | | 500- μ metal foil | 15,000 |
| Zr | 40 | 15.69 | 17.78 | 17.66 | 17.97 | 100- μ metal foil | 14,500 |
| Mo | 42 | 17.37 | 17.48 | 19.60 | 19.96 | 50- μ metal foil | 18,000 |
| I | 53 | 28.32 | 28.61 | 32.29 | 33.05 | 50 g crystalline iodine | 4,400 |
| Ce | 58 | 34.28 | 34.72 | 39.26 | 40.24 | ~1 g $\text{Ce}(\text{NO}_3)_4$ | 9,900 |
| Nd | 60 | 36.85 | 37.36 | 42.27 | 43.34 | ~1 g Nd_2O_3 | |
| Er | 68 | 48.22 | 49.13 | 55.67 | 57.12 | ~1 g Er_2O_3 | 4,500 |
| W | 74 | | | | | 100- μ metal foil | 8,700* |
| Au | 79 | | | | | 250- μ metal foil | 8,500* |
| U | 92 | | | | | 25- μ metal foil | 19,500* |

* These figures refer to L x-rays in the case of W, Au, or U samples.

justed so that the full range of the analyzer could be used to show the complex structure of the K x-rays of each element. X-ray energies were taken from tables (see Table 3).

The results are shown in Fig. 7. We observe in each element a pattern of four peaks, consisting of the $K\alpha_2$, $K\alpha_1$, $K\beta_1'$, and $K\beta_2'$ groups. The $K\beta_1'$ and $K\beta_2'$ peaks contain unresolved components. The resolution, expressed in full width at half maximum, is 1.1 keV.

To demonstrate that x-rays of neighboring elements could be resolved, we performed several experiments in which 0.01-cm foils of two elements were placed side by side in the sample position. Figure 8 shows the result of

simultaneous measurement of x-rays of gold and platinum, elements 79 and 78, respectively. In this case, the $K\alpha_2$ group of gold is equal in energy to the $K\alpha_1$ group of platinum, so a three-peaked $K\alpha$ structure is observed with the central peak largest. In the $K\beta$ peaks, the $K\beta_2$ group of gold is clearly resolved, but the $K\beta_2$ group of platinum falls beneath the $K\beta_1$ group of gold.

In Fig. 8 we also show the results of a similar experiment with gold (element 79) and lead (element 82). In this case the $K\alpha$ groups of lead fall between the $K\alpha$ and $K\beta$ groups of gold, and a clear resolution of all eight peaks is achieved.

The possibility of detecting an element in aqueous solution was demon-

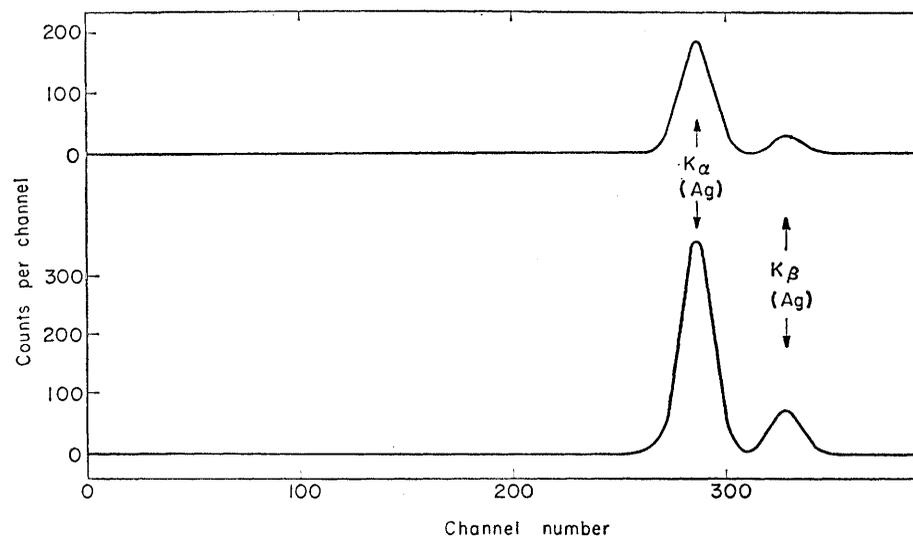


Fig. 5. Characteristic K x-rays of silver excited in dilute solutions of AgNO_3 by 60-keV γ -ray of ^{241}Am . Americium-241 source strength, 10^8 dpm. Lower curve: 0.5 g silver in 5 ml of water held in cellulose nitrate tube. Data collection time, 2 minutes. Upper curve: 10 mg of silver in 1 ml of water. Data collection time, 7 minutes plus 7 minutes background subtraction with sample replaced with 1 ml of pure water. Lithium-drifted silicon detector.

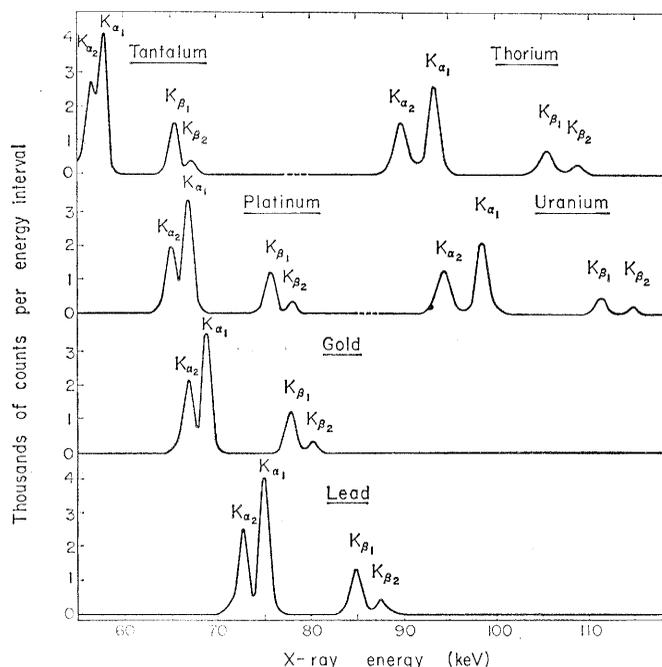
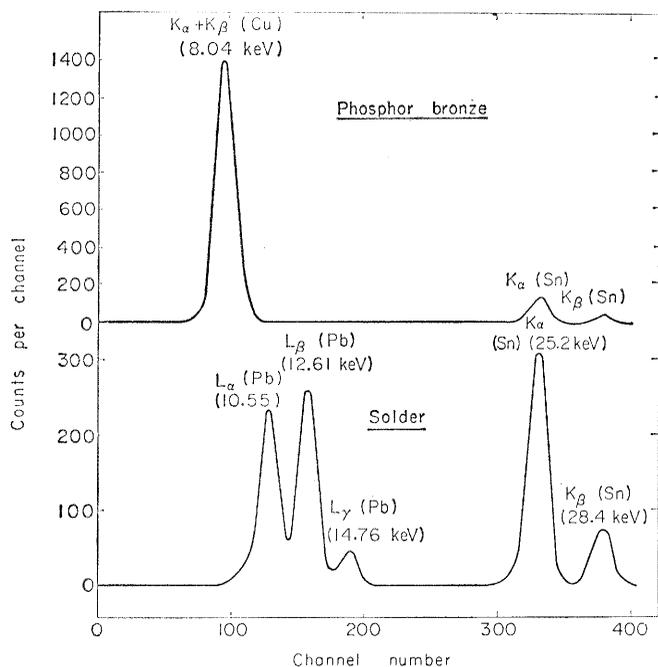


Fig. 6 (left). Analysis of samples of solder and phosphor bronze. Figures show x-rays excited in sample by ^{241}Am source and analyzed by lithium-drifted silicon detector. Counting time, 2 minutes. Fig. 7 (right). K x-ray spectra of tantalum, platinum, gold, lead, thorium, and uranium recorded by lithium-drifted germanium semiconductor. The x-radiation was excited in metallic foils of these elements by γ radiation of ^{57}Co . Counting times were 2 minutes. Data across range of figures taken with 400-channel analyzer. Energy values were taken from tables.

strated in a series of experiments whose results are displayed in Fig. 9. There was no difficulty in detecting the K x-rays of tungsten in a 2-minute excitation of 355 mg, 35 mg, or 17 mg of tungsten in 1 ml of solution of silicotungstic acid. The 17-mg sample contained also 220 mg of gold, and there was still no difficulty in observing the tungsten x-rays in the presence of the tenfold greater intensity of gold x-rays.

Discussion. The present-day technique of x-ray emission spectrography in its most commonly used form is shown schematically in Fig. 10. An x-ray tube is used as a high-intensity source of primary x-radiation. The target material for the electron beam in the tube is chosen to provide photons of the range of energies needed for the analysis of a given group of elements. This x-ray beam impinges on the surface of the specimen to be analyzed, causing excitation of characteristic x-radiation. This secondary x-radiation is scattered from a crystal surface, and by suitable collimation and selection of Bragg angle of reflection, the radiation is analyzed into its component wavelengths. The number of photons scattered at each Bragg angle in a given period of time is registered by a Gieger counter or proportional counter. The goniometer system is operated by a suitable automatic drive and the results

are obtained in the form of a strip chart showing counting rate as a function of angle.

This system has resolving power greater than can be achieved by the semiconductor diode alone, but in a comparison of the two systems, the latter has certain advantages:

- 1) The efficiency of measurement of the excited x-rays, when all intrinsic efficiency factors and geometrical factors are considered, is orders of magnitude greater for the semiconductor diode.
- 2) To achieve the high resolution inherent in Bragg angle scattering, it is necessary to build a carefully machined goniometer system for the accurate measurement of small angles. The semiconductor system requires no goniometer.
- 3) Because of the first-listed advantage, it is not necessary to use a high-intensity x-ray tube for the primary radiation. A radioactive isotope of only moderate intensity (~ 0.1 to 1 mc) will suffice. This means that a compact and much simpler system can be devised. Power supply problems of the x-ray tube are entirely eliminated. The only power required for the semiconductor system is ordinary 120-volt line current. Battery-operated equipment could be devised for remote or field operation.
- 4) The semiconductor system is a

multichannel system, while the traditional system is a single-channel system, that is, the semiconductor system measures all wavelengths simultaneously, whereas the goniometer plus Bragg reflection system requires a single channel scan over the angular range of interest.

5) The germanium diode can measure efficiently the K x-radiation of the heaviest elements. Because of voltage limitation in most x-ray tubes, the K x-radiation of heavy elements cannot be excited and measured in the traditional x-ray spectrometer.

6) The Bragg scattering angle for the x-ray of a heavy element is the same as the second-order scattering angle for the x-radiation of some lighter element. Problems can arise if both elements are present in the same sample. There are ways to deal with this problem, but in the semiconductor system the problem itself does not occur. However, one may expect to contend with the energy coincidence of L radiation of a heavy element with the K radiation of a lighter.

7) The overall simplicity of the semiconductor system should result in a system of lower cost.

It is worthwhile at this point to consider in more detail the overall efficiency of the semiconductor system diagrammed in Fig. 2.

Let N_s be the number of pulses in

Fig. 8 (right). K x-rays of platinum and gold (upper spectrum) and gold and lead (lower spectrum) as recorded by lithium-drifted germanium detector. Counting time, 2 minutes. X-rays excited in metallic foils by γ -radiation of ^{57}Co . Central peak of K_{α} group in upper spectrum shows superposition of platinum K_{α_1} on gold K_{α_2} . In lower spectrum, K_{α} group of lead falls between K_{α} and K_{β} groups of gold.

the output of the semiconductor detector with amplitude corresponding to characteristic K x-radiation of an element in the sample being analyzed. Then,

$$N_s = N_0 \text{Geom}_1 k_{\text{abs}} \omega_K \text{Geom}_2 \text{Eff}_{\text{Det}} - \text{Bkg}, \quad (1)$$

where N_0 = total number of primary photons; Geom_1 is a geometry factor giving the fraction of photons emitted by the radioactive source which reaches the sample; k_{abs} = fraction of primary photons reaching the sample which is absorbed in the K-electron shell of the element sought in the sample; this is computed from the photoelectric mass absorption coefficient and the thickness of the sample; ω_K is the fluorescent yield, that is, it is that fraction of K-electron vacancies which gives rise to K x-rays; Geom_2 is a geometry factor giving the fraction of characteristic x-rays which reaches the detector; Eff_{Det} is the detector efficiency, including window effects, for radiation of the specific energy of the K x-rays; and Bkg is the number of output pulses contributed by background and instrumental effects of all types.

Equation 1 assumes that the absorbing sample is so thin that no correction need be made for self-absorption in the sample or for the various absorption and enhancement effects which are encountered in thicker samples of variable chemical composition.

The factor ω_K is outside our control but is not small. It varies from 0.12 at element 20 to 0.96 at element 90. The geometry factors can be made 10^{-3} to perhaps 10^{-1} . The attractiveness of the system stems from the fact that detector efficiency is close to 100 percent and that k_{abs} can be made high for a particular element or group of elements by proper choice of primary radiation.

Photon absorption coefficients are well known as a function of photon energy and of the atomic number of the absorber (6). In particular, it is known that photoelectric ejection of an electron from a particular electronic shell occurs most strongly just above the binding energy of the electron.

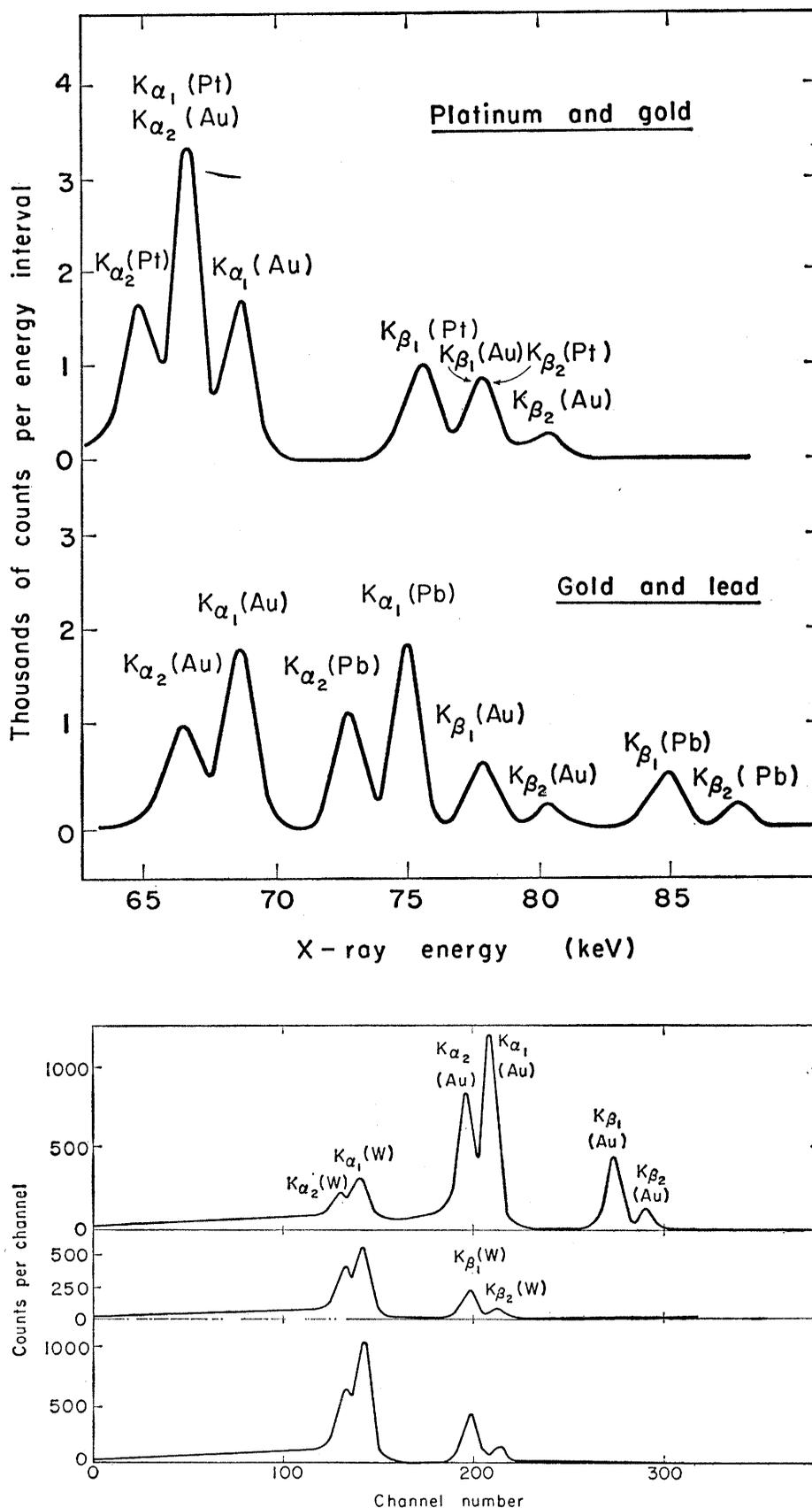


Fig. 9. Analysis of x-radiation emitted by aqueous solutions containing tungsten (element 74) and gold (element 79). Bottom curve: 1 ml of solution of silicotungstic acid containing 350 mg of W. Center curve: 1 ml of solution of silicotungstic acid containing 35 mg of W. Top curve: 2 ml of solution of silicotungstic acid containing 17 mg of W and 220 Mg of Au. Characteristic x-radiation excited by ^{57}Co . Counting times, 2 minutes plus 2 minutes background subtraction with pure water solutions in sample position. Lithium-drifted germanium detector was used in all cases.

Table 3. K x-ray energies of several heavy elements.

| Element | Atomic number | X-ray energies (in kev) | | | |
|---------|---------------|-------------------------|----------------|---------------|---------------|
| | | K_{α_2} | K_{α_1} | K_{β_1} | K_{β_2} |
| Ag | 47 | 21.99 | 22.16 | 24.94 | 25.45 |
| Ta | 73 | 56.28 | 57.53 | 65.22 | 67.01 |
| W | 74 | 57.98 | 59.32 | 67.24 | 69.10 |
| Pt | 78 | 65.12 | 66.83 | 75.75 | 77.88 |
| Au | 79 | 66.99 | 68.81 | 77.98 | 80.18 |
| Pb | 82 | 72.81 | 74.97 | 84.94 | 87.36 |
| Th | 90 | 89.96 | 93.35 | 105.61 | 108.7 |
| U | 92 | 94.66 | 98.44 | 111.3 | 114.6 |

Hence, to emphasize the emission of x-rays of a particular element, the exciting radiation should have such an energy. With the wide variety of available radioactive isotopes, it is possible to select one particularly suited for the analysis being undertaken. Hence, many possibilities for selective control of sensitivity are available.

Applications. The most obvious application of the ideas and results presented here is the construction of a system for the routine analysis of samples. Our experimental apparatus was far from ideal for this purpose and the order of sensitivity which our figures demonstrate is not a true rep-

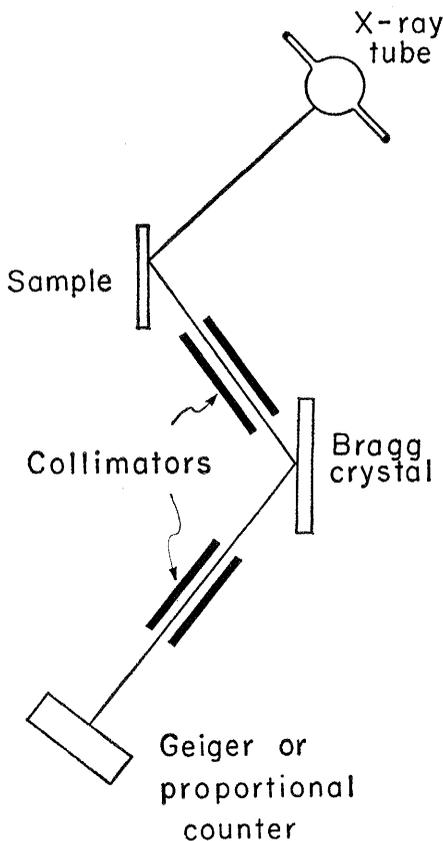


Fig. 10. Schematic diagram of conventional x-ray spectrograph.

resentation of the ultimate capability of a properly designed system. Considerable thought would need to be given to the mounting and housing of the semiconductor diode, the strength and configuration of the radioactive source, the optimal thickness and placement of shielding, and so forth.

A semiconductor x-ray emission spectrograph would be an invaluable instrument for rapid, nondestructive qualitative analysis of materials. The method could be developed into a quantitative technique for measurement of the elementary composition of materials for the milligram and microgram level.

In addition to this, however, one can suggest numerous attractive applications stemming from the simplicity of the system. For example, one could design a rugged miniaturized probe consisting of radioactive source, semiconductor diode, a preamplifier, and a coolant, which could be placed in test holes in mines, in oil well drill holes, in chemical plant process streams, or in other remote or confined locations. The signal from the preamplifier could be cabled to the bulky part of the apparatus consisting of amplifiers and pulse-height analyzing equipment which could be located tens of hundreds of feet away. Applications to space science might be possible. For example, a semiconductor x-ray emission spectrograph would be as feasible as some devices now under consideration for analysis of the surface of the moon.

Various x-ray techniques now used for measurement of film thickness or of the thickness of plated materials could be redesigned with this simpler apparatus.

The solutions emerging from columns of absorbent materials or columns of ion exchange resin could be monitored by a semiconductor x-ray emission spectrograph to determine the identity and quantity of material eluting from the column. It would also be possible to design a unit for scanning a column of ion exchange resin, a column of any chromatographic absorbent material, or pieces of absorbent paper used in such analytical techniques as filter-paper chromatography, paper electrophoresis, and so forth. In such a unit the radioactive source would be highly collimated and would be mounted on a mechanism which could scan segments of the chromatographic column or paper. The semiconductor detector would also travel in a suitable

geometrical relationship to the primary radioactive source.

There is a general analytical technique known as x-ray microanalysis by means of electron probes (7) which could be modified with advantage to incorporate the new system. In this analysis technique an intense beam of electrons is focused on a tiny spot of a specimen and the characteristic x-rays of the elements located at the micro-spot are excited. The semiconductor x-ray spectrometer would be an excellent device for analysis of this radiation.

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8. This work was made possible by recent work on the use of field effect transistors in low-noise preamplifier circuits carried out by E. Elad and M. Nakamura. It also is based on development work on detectors carried out in this laboratory by F. S. Goulding, W. L. Hansen, R. Lothrop, and H. E. Smith. G. Armantrout of the Livermore Laboratory supplied excellent germanium detectors. This research was done under the auspices of the U.S. Atomic Energy Commission.

22 November 1965