The Semiconductor Revolution in Nuclear Radiation Counting

Applications of nuclear radiation have entered a new era with the advent of germanium and silicon counters.

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The measurement of the absorption and emission of electromagnetic radiation of discrete wavelength is one of the most pervasive pursuits in analyzing the structure of matter. Radiations of specific wavelengths are absorbed to change a structural configuration to one of higher energy, and emitted in the reverse process. Between the different domains of structure (molecules, atoms, nuclei) the wavelengths of radiations differ tremendously, and it is not even possible to discuss the experimental aspects as a single subject. Nevertheless all such studies correctly bear the title *spectroscopy*, and they have some common objectives: to measure the radiations with highest possible discrimination of wavelength, and to obtain the greatest sensitivity in determining the intensities of these photon lines.

Once the "spectroscopy" of a system has been determined, important dividends accrue which are unrelated to considerations of structure per se. The distinctive features of spectra make them ideal analytical tools and indeed permit determinations which often can be made in no other way. Here we review some applications of nuclear gamma-ray spectroscopy which followed the discovery that certain semiconductor materials could be used to help fill a void in existing techniques. We also say something of what these new techniques have contributed toward the elucidation of nuclear structure.

The nuclear spectroscopist, almost uniquely, is concerned with the measurement of charged particles (high-energy electrons, alpha particles, protons, and a multitude of others) in addition to photons. For this purpose magnetic spectrometers have long served as instruments of high resolving power and general applicability; but there have been important applications of semiconductor counters in this domain also. This subject, too, is touched upon.

Goals and Tools of Gamma-Ray Spectroscopy

The demands upon gamma-ray spectroscopy are severe even in light of the new developments. Typically, spectra are complex, and the experimenter needs to resolve all the gamma-ray lines present and measure their intensities if he is to make a full analysis of the energy-level structure. He must also make a good many auxiliary measurements, which in themselves may be major pieces of research.

The paramount objectives for proper instrumentation are (i) high-energy resolution and (ii) high efficiency. Unhappily, methods which excel for one are inadequate for the other. We briefly state some of the problems in order to show that the most useful instrument is one which excels for neither of these objectives.

In the typical gamma-ray spectrum the gamma rays may cover an energy range from a few thousand electron volts (kev) to several million electron volts (Mev) (*1*). The relative intensities of the gamma-ray lines may vary over a range of thousands, and some substances of great interest cannot be made in large amounts. An instrument which is inefficient will not measure the very weak lines, but the problem of resolution also enters here. If peaks are sharp, the weak transitions have a better chance of standing out above the tailing from the intense transitions (*2*) and the background from extraneous sources. Finally, speed in obtaining data is often an important consideration. Many radioactive species have half lives too short for making prolonged measurements, and, more generally, the volume of information needed for a thorough study is discouraging if the experimental methods are slow.

Two methods have been used which meet the criterion for high resolution quite well. One of these, diffraction by a crystal, gives absolute energies and has been used in establishing a number of gamma-ray energy standards and in a number of excellent studies. It is not of general applicability, however, because an intense source is required and the time needed for measurement is long. Both the resolution and the efficiency decrease fairly rapidly with increasing photon energy; thus, not only is it tedious to measure gamma rays with energies as high as 500 kev but the resolution is actually poorer at these energies than that obtained with some methods of higher efficiency.

An indirect method for measuring gamma-ray spectra is to analyze, with a beta-ray spectrometer, the photoelectrons produced in a thin "radiator" upon which the gamma rays impinge (*3*). An instrument of high resolution has a low transmission, and in a thin foil the production of photoelectrons is small. The number of photoelectrons at the detector is roughly 10^{-7} of the number of gamma rays at the source. Such systems have given excellent results, but they cannot be used for weak lines. For best resolution, data accumulation is slow because the spectrum must be scanned one point at a time. The resolution (*4*) obtainable is about 0.3 percent of energy of 1 Mev, a value considerably better than that for a crystal diffraction spectrometer at this energy.

It is small wonder that the scintillation counter (sodium iodide) spectrometer became so important when it came into general use some 15 years ago. The resolution is relatively poor (peak width of 6 percent at 1 Mev, 18 percent at 100 kev), but the efficiency approaches 100 percent, and the instrument is a "multichannel device" —that is, the entire spectrum can be recorded at one time. With the development of this spectrometer it be-

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came possible to measure gamma rays quickly, the instruments were produced commercially, and there was an explosive growth in applications. Despite the tremendous impact which this device has had upon nuclear physics and its applications, the relatively poor resolution was clearly causing experimenters to miss important information. This deficiency is increasingly apparent when one compares results obtained with semiconductor counters. An illustrative comparison is given below. But here it should be pointed out that semiconductor materials so far used (principally germanium) have inherently poorer detection efficiency than sodium iodide.

Neptunium-239 is a beta-ray emitter whose decay populates various excited states of plutonium-239, giving rise to gamma rays from these levels. A spectrum of gamma rays obtained with a scintillation spectrometer is shown in Fig. 1. For a particular aspect of the structure of Pu^{239} the weak groups labeled 0.44 and 0.49 Mev were of interest. (Note the logarithmic scale of intensities.) When this energy region was examined with a germanium counter spectrometer, in the summer of 1964, the data shown in Fig. 2 were obtained. As may be seen (Fig. 2), 12 lines showed up; from their positions and intensities it was possible to make a detailed analysis and interpretation such as could not possibly be made from the data of Fig. 1. In Fig. 2 the relative importance of resolution over efficiency is readily seen. The efficiency of the germanium counter was still good enough for seeing those gamma rays which have about 1/1000 the intensity of the most prominent line, at about 280 kev (not shown in Fig. 2). To measure these weak lines with a crystal diffraction spectrometer would require a source of Np^{239} of some 1000 curies and perhaps take several hundred times as long.

The two factors, resolution and efficiency, for several types of spectrometers are presented in Figs. 3 and 4. Characteristic of the rapid developments in semiconductor counter technology is the fact that the curve for germanium in Fig. 3 and the resolution shown in Fig. 2 are already out of date. In Fig. 3 the value for the line width for photons of 300-kev energy is shown as 3 kev, and this resolution has now been bettered by a factor of about 2.

Properties of Semiconductor Spectrometer

There is not space to discuss here in detail the way in which a semiconductor counter works and what sets it apart from other counters. Briefly, it is a device for converting ionization produced in the crystal into an electric pulse. This is amplified and registered, according to energy, by a pulse-height analyzer. By comparison with a gaseous ionization chamber, the pulse of electrons collected is greater, the peaks are more discrete (that is, resolution is better), and the collection of ions is more rapid. These are all factors of great importance. Since we are interested in events caused by the photons which accurately mirror their energies, we are concerned primarily with the photoelectric effect. The cross section for the production of photoelectrons by particular photons increases with atomic number, and it is here that the semiconductor counters fall short of the efficiency of sodium iodide scintillators. The only materials used successfully so far are silicon and germanium, both elements of rather low atomic number. In the future, emphasis will surely be directed toward use of heavier elements; it is now being placed, with satisfactory results, on the construction of larger and larger counters, to partially offset the intrinsic disadvantage of the lighter material. The science and the art involved are by no means trivial, so rapid development in these directions is not assured.

Essentially a counter may be viewed as a block or wafer of material with an electrode attached to opposite faces and a certain voltage maintained across

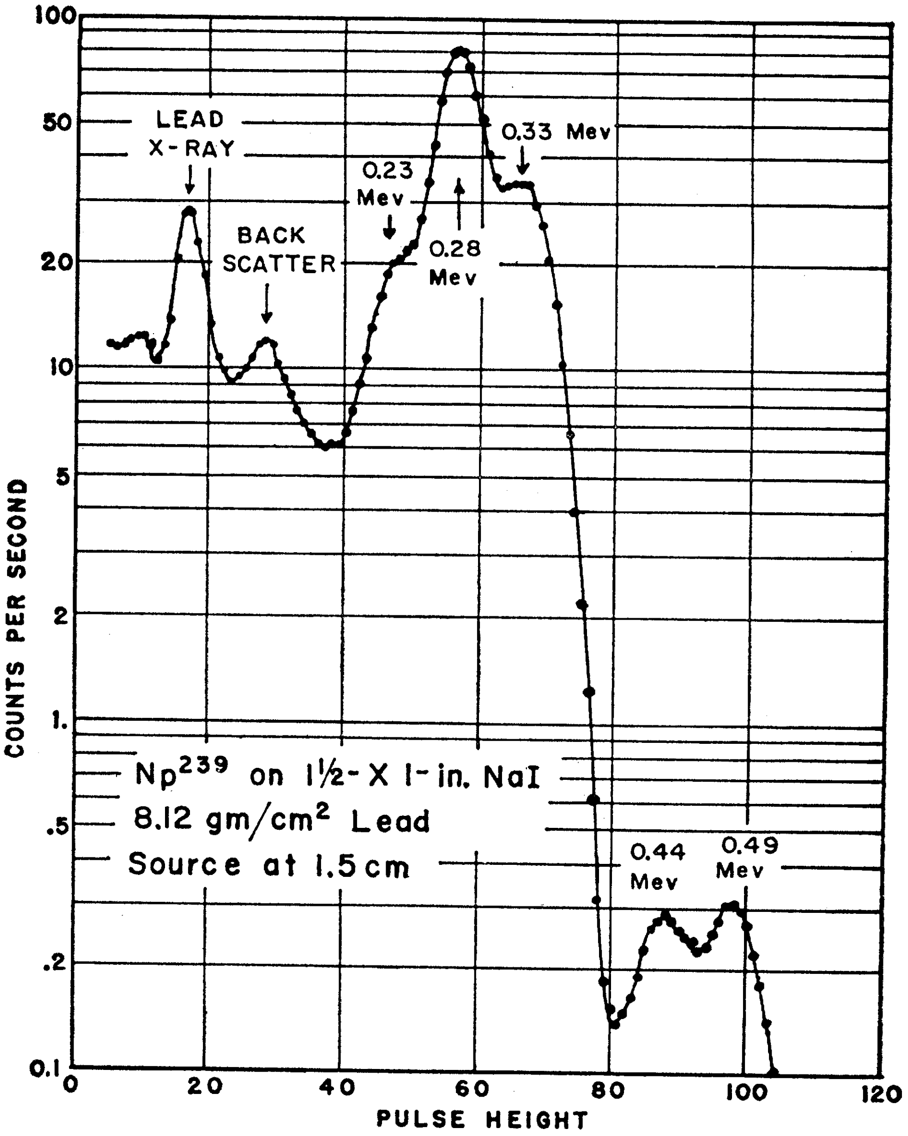


Fig. 1. Gamma-ray spectrum of Np^{239} from a sodium iodide scintillation spectrometer. [From Lefevre, Kinderman, and Van Tuyl (*14*)]

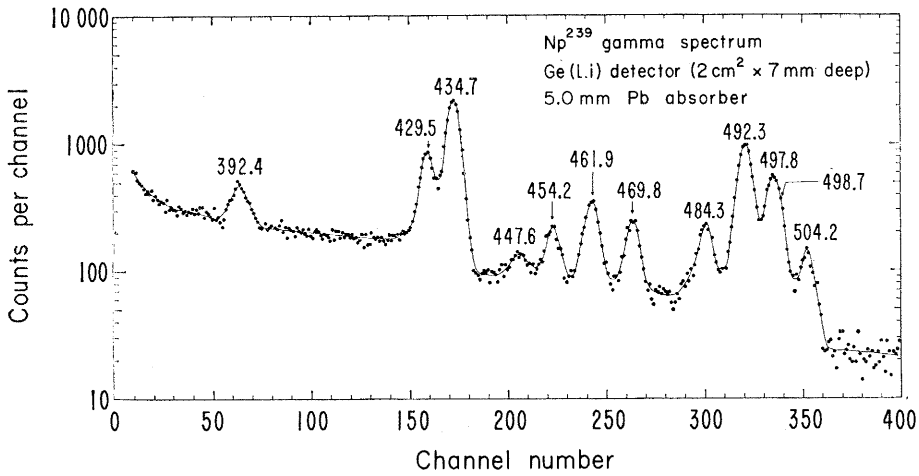


Fig. 2. Portion of the gamma-ray spectrum of Np^{239}. Energies are given in thousands of electron volts. (The peak widths attained in this spectrum have been decreased by a factor of ~2 in the 2 years since this measurement was made.) [From Davis and Hollander (*15*)]

the block. Ionization within the block results in a movement of charge carriers in the direction of the potential gradient. It is obvious that a metal will not serve as a counter because a large current will flow through a metal without induced ionization. Similarly, it is important that the semiconductor have very few free carriers, since the ionization pulse from a single photon is not very great.

The huge advantage that the semiconductor counter has over other devices lies in the small amount of energy required to create an ion pair. In germanium, the photoelectron from a gamma ray of 300-kev energy produces about 100,000 ion pairs. If these can be collected before they are trapped, the statistical dispersion will produce a peak width from this source alone of about 1 kev. Actually the problem cannot be treated so simply, and there is reason to believe that the limiting width will be even smaller than this. Until very recently the amplifier noise and the leakage currents have been clearly limiting, but, as mentioned in the discussion of Fig. 2, a peak width of 1.5 kev has been attained. In detector materials which produce fewer ion pairs, or in those (like sodium iodide) which depend upon collection of light, the statistical factors are, in principle, limiting. A scintillation counter-photomultiplier spectrometer gives a peak width of 25 kev for a 300-kev photon. The reasons for this large spread are rather complex but can be summarized in the statement that about 300 electron volts of energy absorbed in the crystal are required to produce one electron at the cathode of the photomultiplier tube.

The difficulty in obtaining good semiconductor counters results from the difficulty of collecting all the electrons produced and of eliminating currents not connected with the photon-induced ionization. We will not go into the technical difficulties; suffice it to say that high-purity germanium must be further treated to reduce the number of free carriers, and the counters must be operated at reduced temperatures (usually liquid-nitrogen temperature) in order to reduce thermal noise. Figure 5 is a photograph of a counter assembly.

Studies in Nuclear Spectroscopy

Since our object here is to introduce many readers to the semiconductor counter, our emphasis in discussing nuclear spectroscopy is on the contrast between results obtainable with this and with other techniques, not on the technique itself.

The partial gamma-ray spectrum of Np^{239} showing weak transitions unobservable by other techniques was mentioned in connection with Fig. 2. Ten of these 12 photon lines established four new energy levels, simply through the matching of energy differences with those of known lower-energy states. For example, the photons of 492.3-, 484.3-, and 434.7-kev energy fit well for transitions between a level at 492.3 kev and (i) the ground state, (ii) the 7.9-kev state, and (iii) the 57.3-kev state, respectively. The latter group of states is well known from other studies. To learn the nature of the new states was of course the focal point of the investigation. The spacings of the four newly established states gave a clue that they might be members of a nuclear rotational band whose base state has total angular momentum 1/2. Theory also predicts what the *relative* intensities of the gamma rays should be for that assignment, and the experimental evidence gave further support. By using published data on the electron spectrum from the same nucleus, it was possible to set certain limits on the internal conversion coefficients (defined below) for the gamma-ray transitions, and this further limited the *type* of rotational band involved. Finally, the *absolute* intensities of the lines gave information on the beta-decay population to these states, which in turn gave further detailed information on the nature of these states.

The foregoing example does more than show that gamma-ray spectroscopy can be done well with semiconductor counters. It shows that a nuclear system which had been investigated almost exhaustively by other techniques quickly yielded new information. Even though these counters have been used for only a very short period of time, an impressive list of examples could be cited.

We will mention just one other study involving a radioactive nucleus. Alexander, Boehm, and Kankeleit (*5*) made an elegant and exhaustive study of the energy levels of lutetium-177—a study in which crystal diffraction spectrometry played a central role. They used a 100-millicurie source, and the measurements required 6 months. The spectrum was quite complex, consisting of more than 40 gamma rays, and was interpreted neatly in terms of a few highly revealed rotational bands.

The same spectrum was later measured by Blok and Shirley (*6*) with a germanium spectrometer; they used a source of less than 1 millicurie, and the measurement took 8 hours. Their measurement confirmed the earlier work in great detail, but, in addition, they looked for a "missing" line presumably too weak to have been detected by other methods. This was found without special search, and its position in the energy-level sequence was established unequivocally. Using two germanium counters, they were able to show that this line was in coincidence (*7*) with particular other gamma rays which should lie below it in the decay sequence. This type of experiment is mandatory for many decay-scheme studies and demands high efficiency; in this case a transition too weak to be seen even in *direct* measurement by other methods was involved.

Recently this spectrum has been measured under conditions similar to those of Blok and Shirley with a germanium spectrometer of increased resolution (*8*). A part of the spectrum is shown in Fig. 6. This spectrum revealed four new lines, not seen in either of the other studies, which fitted perfectly into the level scheme of Alexander *et al.* In addition, ten other new lines, still weaker, were found; these have not yet been definitely interpreted. The peak widths for the peaks of Fig. 6 are about 1.5 kev; this resolution is at least three times as good as that achieved through crystal diffraction at this energy. More important than the increased resolution was the vastly improved peak-to-background ratio. In the diffraction spectrometer study this ratio was about 1 to 1 for one of the weakest lines seen; in Fig. 6 it is 40 to 1 for the same peak! This favorable peak-to-background ratio not only makes it easier to observe weak groups but makes it possible to determine their intensities more accurately. This is of great importance in the theoretical interpretation of the energy-level structure.

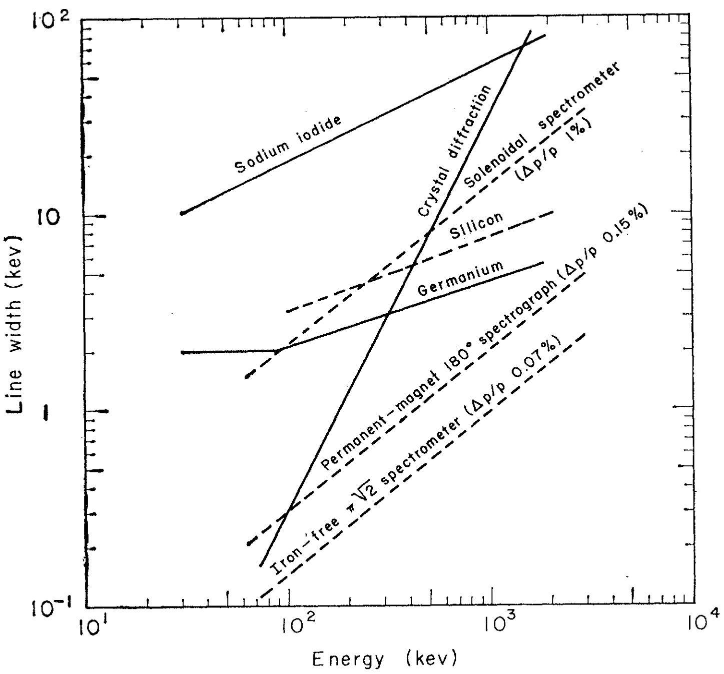
Radioactive decay is by no means the only basis of measurement in nuclear spectroscopy. Valuable information is being obtained from the analysis of radiation and particles produced in nuclear reactions, usually accelerator-induced. Most such experiments are carried out while the beam is turned on, a situation in which there can be considerable extraneous background radiation. For discriminating against this background radiation, instruments of high resolution have a distinct and obvious advantage, and semiconductor counters have been used to good advantage here also. Although in-beam experimentation and the use of semiconductor counters as spectrometers are both quite new techniques, important results have already been obtained in abundance, and the prospects for the future are exciting.

Auxiliary Aspects of Nuclear Spectroscopy

There are many types of experiments involving high-energy photons in which a spectrometer of moderate efficiency and high resolution is an asset. A few examples will illustrate the diversity of applications.

Low-temperature nuclear orientation. The magnetic moment of a nucleus interacts weakly with that of the atomic electrons. At sufficiently low temperatures in a magnetic field the nucleus becomes oriented through this interaction, and gamma rays which are emitted have angular anisotropy patterns which depend upon the angular momentum of the initial and final nuclear states. The effects often are not large, and, if there are gamma rays which cannot be resolved, the observed angular anisotropies are likely to be "washed out" or impossible to interpret for other reasons.

Nuclear orientation studies made with scintillation spectrometers have given valuable information in cases where the gamma-ray spectrum was extremely simple. In the more general situation, better resolution is required.



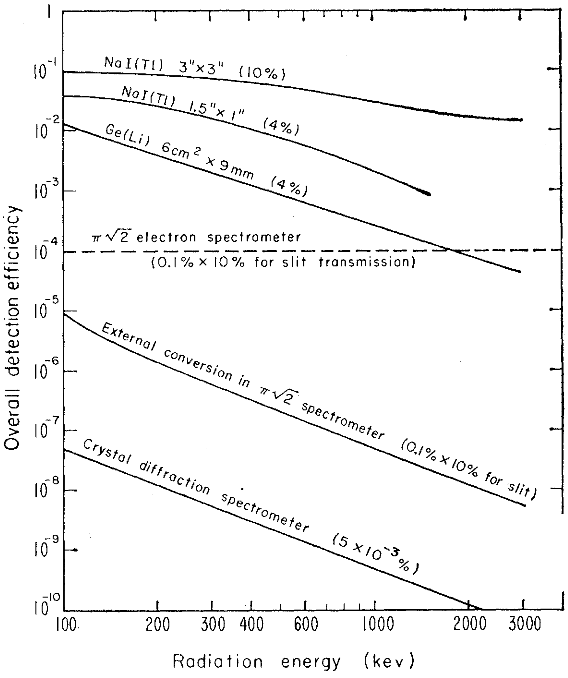
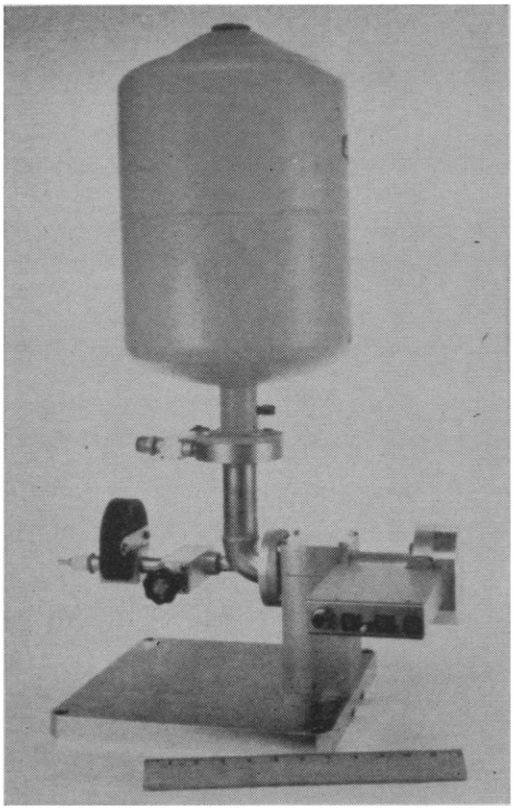


Fig. 3 (left). Resolution of various spectrometers. In addition to curves for four photon detectors, curves for *electron* resolution from three types of beta-ray spectrometers, used in measurements of conversion electrons, are shown, with the momentum resolution ($\Delta p/p$) given in parentheses. Not shown are performance characteristics of beta-ray spectrometers as used with secondary electrons (photoelectrons) (see text). Because of problems not associated with the magnet, the line widths attainable are not as good as the curves of this figure indicate. The resolution now attainable with germanium counters is better than that shown by a factor of at least 2. [From J. M. Hollander (*16*)] Fig. 4 (right). Approximate efficiencies of spectrometer systems. The overall detection efficiency shown (ordinate scale) is the product of the intrinsic efficiency and a geometric factor (solid angle subtended from source to detector). The geometric factors commonly found are shown in parentheses. [From J. M. Hollander (*16*)]



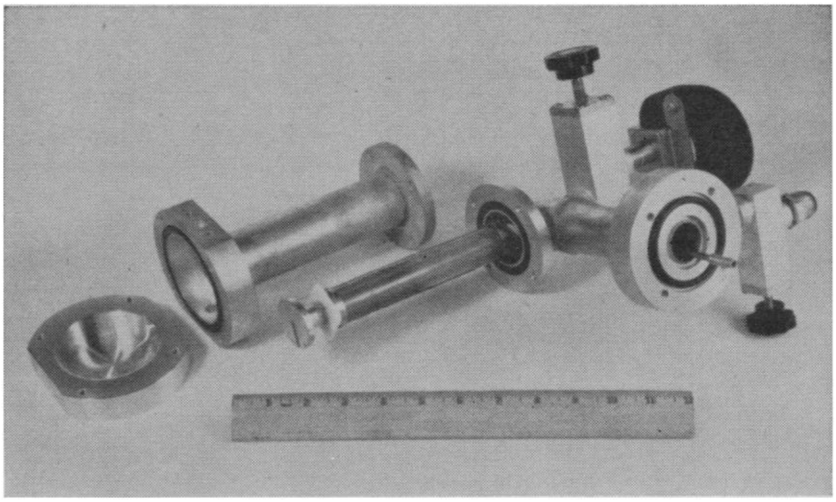


Fig. 5. Typical basic unit for a semiconductor counter. (Left) Assembled unit, showing liquid-nitrogen reservoir, ion pump at left, detector housing and preamplifier at right. The pulse-height discriminator is not shown. (Above) Major components of the semiconductor counter. The component immediately above the scale is the cold finger; the semiconductor detector is clamped onto disk at left. The stand, preamplifier, and reservoir are not shown.

Some highly successful experiments made with the newly available germanium spectrometers have now been reported, and the potentially broad usefulness of this type of experiment seems about to be realized.

The low-temperature, nuclear-orientation experiment is only one of a number in which the directional emission of radiation is used to probe the currents of electric charge and the mechanical moments of nuclear systems. Some of these experiments are as exotic as they are ingenious; all benefit from the availability of high-resolution spectrometry.

Mössbauer effect. The cross section for the absorption of a photon by a nucleus depends with extreme sensitivity upon the matching of its energy with the energy of excitation between two nuclear states. This effect has been extensively explored, for it was recognized that the resonances obtained reflect the finest distinctions of chemical environment in which the atom sits. In practice, the proper gamma-ray energy is obtained by using the same nuclear species for the absorber and for the source of the gamma rays and eliminating the largest source of mismatch, the small recoil energy of the emitting and absorbing systems. This is the "Mössbauer effect." The resonances are then observed by shifting the photon energy ever so slightly, through the Doppler effect.

Although the technique is, in first principle, broadly applicable, it is limited on two scores. The natural width of the photon line is important, and this is related to the lifetime of the state giving rise to the gamma ray. Therefore, in practice, one must be lucky enough to find the right gamma-ray-emission half life in the substance of interest. Further limitation arises from the problem of gamma-ray resolution by the detector which measures the degree of absorption as a sweep is made through the resonances. A number of otherwise suitable "Mössbauer nuclei" had other gamma rays or x-rays of energy sufficiently close to that of the particular usable transition that they were thought useless or at least of limited use. The availability of germanium and silicon counters will surely broaden substantially the scope of this extremely sensitive technique, as has already been demonstrated in a few instances.

Internal conversion coefficients. As mentioned above, the ratio of the emission rate of an orbital electron (nonradiative transition) to the emission rate of a photon for the same transition is an extremely valuable index of the type of transition involved. The index number is called the internal conversion coefficient, and it can be calculated with satisfying reliability. The detail of information which one can obtain from such measurements is strongly dependent upon the accuracy with which conversion coefficients can be measured. High accuracy is by no means easily achieved because measurement of the electrons and of the photons requires two different types of instrumentation, each with its own resolution and intensity-calibration problems. Until recently the electron lines could be measured with sufficient resolution and accuracy only through point-by-point scanning with a magnetic spectrometer.

In the development of semiconductor counters it was found that a silicon counter coupled with a pulse-height discriminator serves as an electron spectrometer of high efficiency (weak sources may be used) and of sufficiently high resolution to warrant wide application. The electron peak widths so far obtained range from about 1.5 kev at electron energy of 100 kev to approximately 3.5 kev at electron energy of 1 Mev. Although these values are considerably poorer than the corresponding values obtained with a good magnetic spectrometer, the resolution is sufficient for separating the majority of spectral lines. A simple conversion coefficient instrument has been built in which the electrons are measured

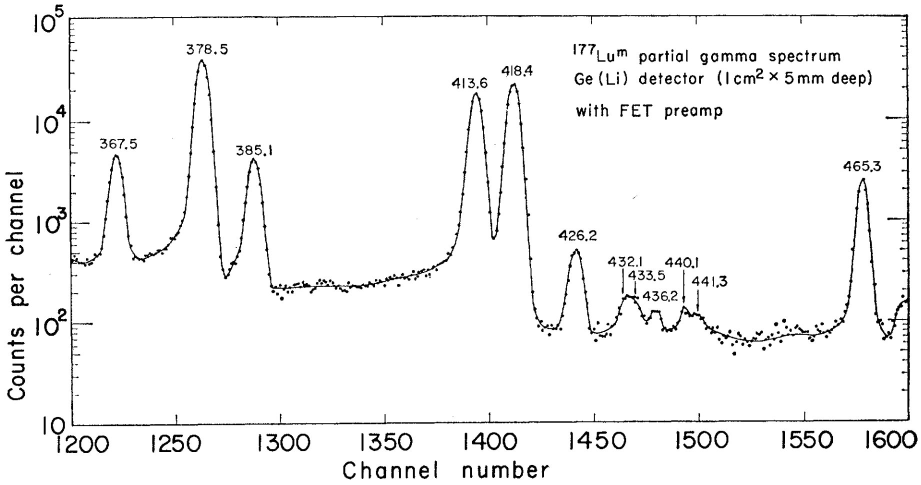


Fig. 6. Partial gamma-ray spectrum of lutetium-177 (metastable state) obtained with an improved germanium spectrometer. Note that the entire section shown covers a range of only 100 kev. [From Haverfield *et al.* (*8*)]

with a silicon detector and the gamma rays are measured with a germanium detector, simultaneously (*9*). Each part of the system must be calibrated, and there are other problems which make the accuracy of determinations somewhat lower than that achieved in special cases by laborious methods. Nevertheless, data may be obtained so much more rapidly with this technique than with other methods, and such weak sources may be used, that a modified version of this instrument is bound to come into general use. Conversion coefficients are among the most valuable indexes of nuclear structure in use.

The conversion of nonradioactive atoms to atoms which are radioactive has become established in the repertory of analytical methods. Detection of the radioactivity with high sensitivity and discrimination is the goal of successful activation analysis. Despite the wide diversity of successful applications of this technique, it is not difficult to generalize on what is required to give it added scope and usefulness. In general the induced spectrum is complex, and for analysis with the sodium iodide scintillation spectrometer, with its rather poor resolution, the specimen is usually subjected to chemical fractionation in order to simplify the spectrum and to accentuate signals coming from weak components. This procedure not only destroys the sample (often an undesirable result) but adds to the time and expense of a determination. Since, in principle, each radioactive substance has a unique spectrum, any instrument which helps resolve the individual signature from other substances cuts down on the amount of auxiliary manipulation necessary.

Figure 7 shows the results of measurement with a scintillation spectrometer and with a germanium spectrometer for a specimen of a sulfate ore which had been subjected to neutron activation (*10*). From spectrum 1 it would be difficult to obtain useful information without some prior knowledge of what was in the sample. Chemical fractionation would of course simplify matters considerably. Analysis of the two spectra (2 and 3) obtained with the germanium spectrometer permitted assignment of the peaks from the raw spectrum. The analytical results are given in Table 1. In this case all the gamma rays are of rather high energy—an energy for which the small germanium counter used is quite inefficient. When larger counters become available this problem will be proportionately alleviated. It should be noted that, at present, if the spectrum is simple and a peak of interest is set far apart from all other peaks, the high efficiency of the sodium iodide counter gives that instrument an advantage from the standpoint of sensitivity.

One should note in spectrum 1 of Fig. 7 that the 819-kev peak from indium was not at all resolved from the 845-kev peak from manganese. Its presence could not be easily detected by repeating the measurement at intervals because the half lives of the two radioactivities are not grossly different. In spectrum 2, not only is the indium peak resolved but the signature is complete, through detection of two other peaks belonging to the same isotope.

Nothing has been said about the precision of analytical results obtainable with germanium counters because such counters add little in this respect. In general, activation analysis does not give high-precision measurements for major components of a sample but finds its great usefulness in the measurement of minor components which cannot be detected easily or at all by other methods.

Radiochemical Tracing and Analysis

The many uses of radioactive tracers do not, broadly speaking, involve detection problems like those discussed here. Generally, a single tracer is added to the system, and any detection method is adequate. However it is not difficult to envision situations involving multiple tracers in which high resolution would be an advantage. No doubt, such situations will arise.

A particular complex mixture of radioactivities does appear in one industry—that concerned with the separation of the fission products from irradiated fuel elements from nuclear reactors. Considerable laboratory effort is expended in following the progress

Table 1. Results of quantitative analysis of sulfide ore.

Element	Amount present (μg)	Sample weight (mg)	Irradiation time (hr)	E_γ (kev)	Concentration (parts per million)*
Mn	6.0	62.9	2	845(Mn^{56})	95 ± 7
In	7.6	62.9	2	1300(In^{116m})	120 ± 5
Ga	3.8	62.0	2	835(Ga^{72})	61 ± 16
Zn	3020	24.5	24	438(Zn^{69m})	(1.20 ± 0.01) × 10^5
As	60	19.0	72	559(As^{76})	(3.16 ± 0.04) × 10^3
Sb	8.2	19.0	72	563(Sb^{122})	430 ± 6
Cu	1240	19.0	72	511(Cu^{64})	.6.50 ± 0.01) × 10^4†
Na	16	19.0	72	1369(Na^{24})	840 ± 25
Fe	3370	19.0	72	1095(Fe^{59})	(1.78 ± 0.01) × 10^5
Au	0.038	19.0	72	411(Au^{198})	2.0 ± 0.2

* Errors shown represent statistical counting error only. † Copper concentration corrected for contribution to 511-kev annihilation photopeak from decay of Zn^{69} and Na^{24}.

of the separation process and in developing improved processes. Quite obviously any analytical procedure which showed up the troublesome fission products without tedious chemical fractionation would be distinctly useful. One case may be cited. An isotope of zirconium and an isotope of niobium are among the most prominent of fission products, and the behavior of these two elements in aqueous-organic systems is somewhat unpredictable because of their many complex ions and their proclivity to hydrolyze. Analysis of the two radioactive substances is difficult because their gamma-ray energies lie close to each other and chemical separation is not easy. The germanium spectrometer does away with the need for time-consuming manipulations by completely resolving the gamma rays.

Elemental analysis of materials through measurement of their characteristic x-rays is a much-used, albeit tedious, technique. With this form of analysis, most elements can be determined by a single method. The basic idea is quite simple. The fluorescence spectrum is excited by photons from an x-ray tube and analyzed by crystal diffraction. The equipment is fairly expensive and measurements are not rapid, but, in general, excellent results are obtained because of the excellent resolution in the x-ray region of photon energies.

Recently the same principles have been employed successfully with different instrumentation (*11*). Instead of the x-ray tube, a small radioactive source is used to excite the x-rays, and, in place of the crystal diffraction spectrometer, a silicon or germanium counter is used. This technique has certain deficiencies as well as great advantages. The high noise level of the counter system makes it impossible, at present, to make measurements of elements of atomic number below about 20. Also, the energy range of x-rays is the range for which the crystal diffraction spectrometer gives clearly superior resolution. This means that the older technique is better when neighboring elements are present in widely disparate amounts.

The feasibility of using semiconductor counters for elemental analysis depended, first of all, on major improvements that were made in the amplifier system, which made possible the resolution of x-rays from neighboring elements. The great advantage of the instrument is the speed with which large numbers of analyses can be made. With a very modest radioactive source, a typical sample may be analyzed in a very few minutes. Another desirable feature of the instrument is its porta-

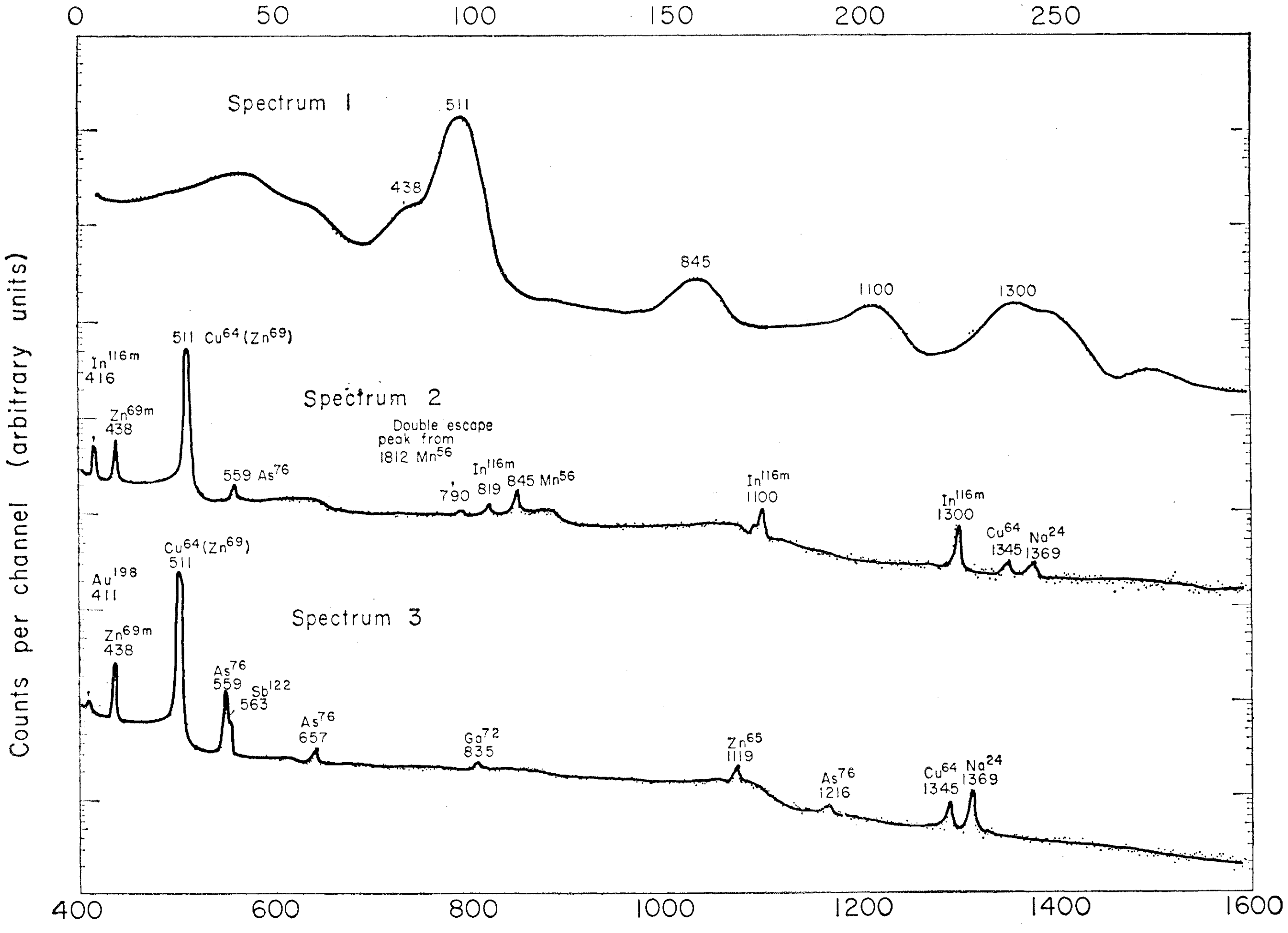


Fig. 7. Gamma-ray spectra of activated sulfide ore. (Spectrum 1) Sixty-minute data accumulation with the 3- by 3-inch (diameter) sodium iodide scintillator 5.2 hours after a 2-hour irradiation of 62.9 milligrams of sulfide ore; (spectrum 2) 60-minute data accumulation with the smaller Ge(Li) detector 4 hours after a 2-hour irradiation of 62.9 milligrams of the ore; (spectrum 3) 120-minute data accumulation with the smaller Ge(Li) detector 24 hours after a 49-hour irradiation of 50 milligrams of the ore. [From Lamb *et al.* (*10*)]

bility. Because of these characteristics one can easily visualize its use for on-line control of an industrial process. It could also be used for field work in mineral prospecting and archeology, where it is often necessary to examine many specimens before segregating them or discarding some of them.

Figure 8 shows the peaks obtained from samples of yttrium and illustrates the sensitivity and resolution obtained for x-rays of about 15-kev energy. The Kβ peak is separated from the Kα peak by 2 kev, an amount which is close to the peak widths. At the atomic number of yttrium, adjacent elements have x-rays differing by only about 1 kev, so it would be difficult to resolve these peaks unless the elements were present in comparable quantities. However, since this measurement was made, resolution higher by a factor of >2 has been attained. For heavier elements the x-ray energies are farther separated, and analysis becomes progressively easier.

Particle Spectroscopy

Fewer individuals are engaged in measuring particles (such as protons) than in measuring gamma rays, and applications of the techniques, beyond the intrinsic nuclear studies, are less widespread in this field. Nevertheless, within a more limited scope, the advent of semiconductor counters has produced changes in particle measurement that are no less startling than the changes it has produced in other areas.

The classical method for measuring charged particles is measurement of their deflection in a magnetic field. This technique is still much used and will no doubt continue to be used because of the extremely high resolution attainable. The new semiconductor counters have introduced new dimensions in particle work because they are inexpensive as compared with large magnets, they have much higher efficiency, and they have increased, by a large factor, the speed with which data are obtained. This last attribute can be determinative for experiments in which a reaction must be studied at varying energies of the bombarding particles and at closely spaced angular settings relative to the direction of the beam. The counters can also be used to identify the types of emitted particles, something that simple magnetic deflection cannot by itself accomplish. Since the absorption of charged particles is not sensitive to the atomic number of the detector material, silicon has been favored over germanium up until now, except for studies of high-energy protons (energies greater than 30 Mev).

Small semiconductor counters are thick enough to absorb most of the particles of interest in particle spectrometry. Protons have the longest range for a particular energy, and those with energies up to 30 Mev are stopped in a silicon counter 5 millimeters thick and a germanium counter less than half as thick.

Nuclear energy levels. Accelerated charged particles may be scattered elastically by the nuclear forces of the target nuclei, leaving the nuclei unexcited. The particles may also excite

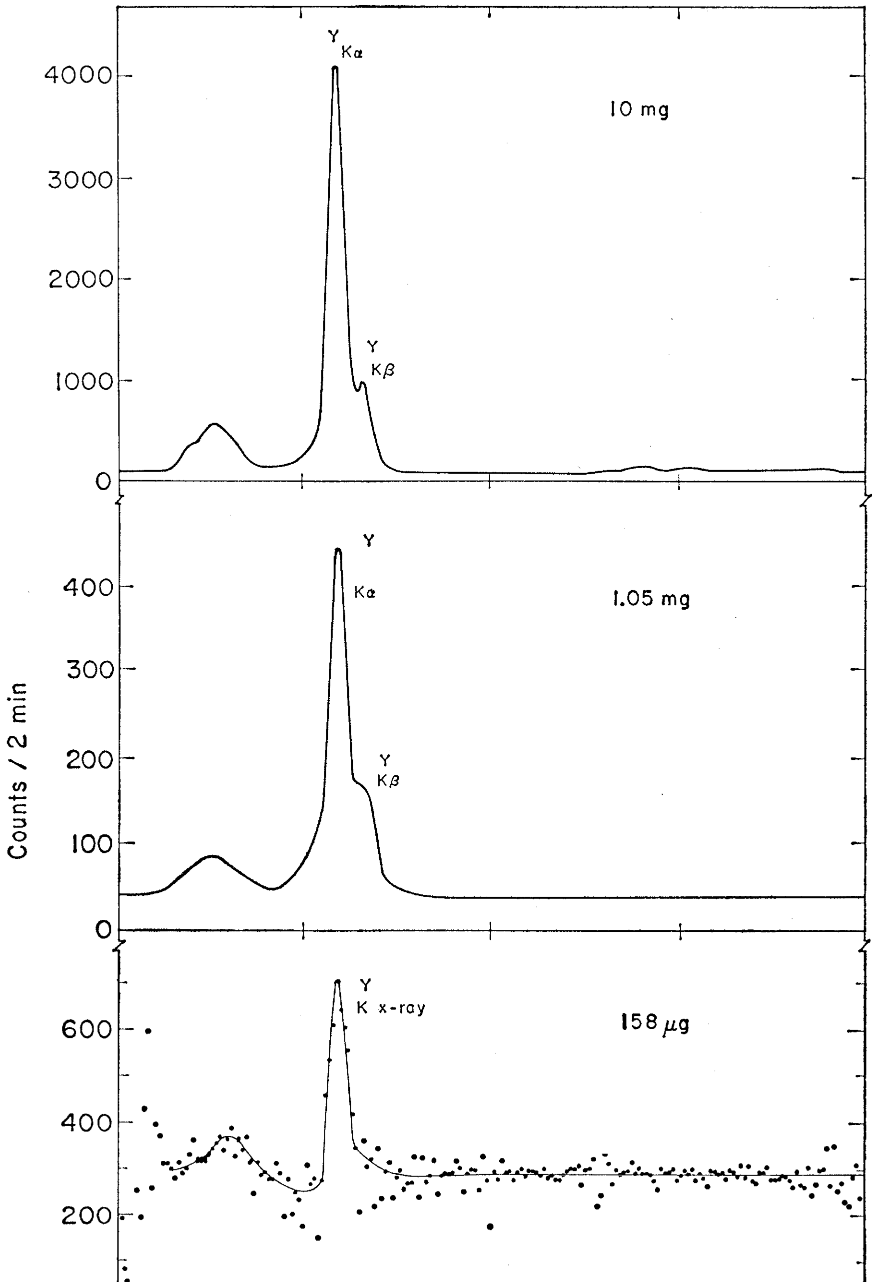


Fig. 8. K-shell x-rays of yttrium excited by radiations of Am^{241} in samples containing 10 milligrams, 1 milligram, and 150 micrograms, respectively, of yttrium and analyzed with a lithium-drifted silicon semiconductor detector. Duration of the analysis for the 10- and 1-milligram samples, 2 minutes; for the 150-microgram sample, 10 minutes. [From Bowman *et al.*, unpublished (*11*)]

the nuclei, in which case the energy of the scattered particles is lowered by an amount equal to the excitation energy. A series of peaks result; the extent to which the energies of these peaks differ from the energy of the elastically scattered peak defines the nuclear states. This form of spectroscopy differs from direct measurement of gamma rays in some important respects. Of fundamental importance is the fact that nuclear states may be reached which are forbidden to radioactive decay processes, or else may be of too high energy to be reached. We have mentioned only inelastic scattering as the means of exciting nuclear states, but these states may be excited by a wide array of other nuclear reactions. For example, deuterons may be absorbed and a series of proton groups emitted. Plainly there is a wide range of nuclear problems open to investigation by such techniques.

The experimental requirements for particle spectrometry are severe, as an example will illustrate. Suppose that protons of 22-Mev energy are scattered, exciting a nuclear state at 4 Mev. The emitted protons will have an energy of 18 Mev. Suppose, further, that there is another nuclear state 50 kev away. If the two proton groups are to be resolved effectively, the resolution of the instrument must be about 0.1 percent for the 18-Mev particles. Until quite recently only magnetic analysis could produce such results.

In a recent report (*12*), energy resolution of 0.1 percent was achieved for protons of energy even greater than 18 Mev. Actually the resolution of the counter itself was better than this value, because a substantial part of the peak width was attributable to the spread in energy of the accelerated particles.

Particle identifiers. For an array of particles emitted from a target, we must measure, at some specific position of the counter relative to the beam axis, (i) the energy, (ii) the mass number, and (iii) the atomic number, if the energy data are to be useable. Simple deflection in a magnetic field gives the momentum per unit charge. Often there is no ambiguity as to the particle involved, but, as more and more details are sought, this is not always the case. A simple ionization detector measures only the energy of the particle, so again identification is not complete.

A particle identifier makes two simultaneous measurements: (i) the rate of energy loss (dE/dx) as the particle traverses a very thin counter, and (ii) the total energy, which is obtained by adding the increment of energy abstracted by the dE/dx counter to the residual energy determined in a thick counter placed behind the thin one. It can be shown that the product of E and (dE/dx) identifies the particle uniquely.

Particle identification when there are many different particles, covering a wide range of energies, is by no means simple. In addition to good detectors, highly sophisticated electronics circuits are required. In this demanding area of research, silicon counters have been used to good effect. The high resolution attainable is of great importance, and they have other properties which are advantageous.

The fact that every particle which reaches the detectors is analyzed gives this system a huge advantage when one is looking for rare events. By using a system somewhat more complicated than that just described, it was found possible to identify and measure the mass of the interesting nucleus helium-8, even though the yield of this particle was 10^7 times lower than the yield of the prominent particles emitted from the target (*13*).

Alpha-particle spectroscopy. Two methods have long been employed for measuring the monoenergetic alpha-groups emitted by many radioactive substances in the heavy-element region. Magnetic spectrometers can give very good resolution, but they have inherent limitations in sensitivity. Gaseous ionization chambers are highly efficient, but, because the resolution attainable with these is poor, they are not used when one is looking for weak groups and groups with energies which are close together. Typically, an ionization chamber gives peak widths of 30 kev (for a 6-Mev alpha group), although considerably better resolution has been reported. A good magnetic spectrometer, with careful preparation of the source, has given peak widths of less than 2 kev, but 6 kev is a more generally attainable value.

Silicon counters are coming more and more into general use as alpha-particle spectrometers. The resolution easily attainable is only about 15 kev, although better resolution than this has been attained. Nevertheless, the difference between this value and that obtainable with an ionization chamber proves huge indeed in work with typical spectra.

Probably the most important feature of silicon counters for work in this area is the fact that they may be readily adapted for making coincidence measurements between alpha particles and gamma rays and electrons. An ionization chamber is not only inferior in resolving power but its ion-collection rate is too slow. Its overall low efficiency for magnetic analysis limits its use in coincidence spectrometry to the more prominent events. With silicon detectors for the alpha particles it has been found possible to measure transitions having less than 10^{-7} the intensity of the main transitions. In working with alpha emitters on problems of nuclear structure it is being found that the rare transitions are just as important as the more prominent ones.

Final Words

One need only scan the foregoing partial list of accomplishments, made possible by the use of semiconductor counters for measuring nuclear radiations, to assess the impact which these are having in broad areas of research. A number of important fields, such as mesonic x-ray investigations, have not even been mentioned. The features of this new form of instrumentation which are already well established are exciting enough, but it would not be rash to predict that the next few years will see further important advances.

References and Notes

1. The deep-shell x-rays are often found to be excited in gamma transitions, and their measurement accompanies that of the gamma rays.
2. In any gamma-ray detector which depends upon ionization, the monoenergetic peak which relates to the photoelectric effect is the "spectral line" we refer to here. Compton scattering is usually a more probable event, and, if scattered photons leave the detector, smaller signals are obtained. This is the principal source of the continuum of signals below the energy of the distinctive peak.
3. It should be mentioned here that orbital electrons are *directly* ejected in nuclear gamma-ray transitions as a process in competition with photon emission. The measurement of these electrons continues to play an extremely important role in nuclear spectroscopy. Such measurements provide a means of obtaining, with high resolution, gamma-ray transition energies, and serve as an adjunct to measurements of the gamma-rays themselves in determining the ratio of radiative to non-radiative transitions, an important index of the nature of initial and final quantum states.
4. The word *resolution* in this article refers to the full width of a peak at half the maximum peak height. This width may be indicated, as it is here, in terms of a percentage of the energy.

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Detection and Measurement of Pesticide Residues

Gas chromatographs with selective detectors have streamlined analysis.

Donald J. Lisk

The term "pesticide residue" refers to deposits of one or more pesticides, and possibly their metabolites, on or below the surface of a biological and often edible substance. A metabolite is an altered pesticide molecule which may be more or less toxic than the original compound that was applied for pest control. Metabolites may result from metabolic reactions in the plant or animal (oxidation, reduction, hydrolysis, esterification) or weathering (ultraviolet light, atmospheric oxidation) which the parent compound undergoes as it comes in contact with a living organism (plant, fungus, insect, or other).

Pesticides can be divided into three categories. (i) Insecticides—to control injurious insects affecting plants, animals, and humans. (ii) Fungicides—to prevent or cure plant diseases caused by fungi. (iii) Herbicides and plant growth regulators—to kill weeds and to make plants grow faster or slower or to alter them in order to increase their benefit to man. Rodenticides, antibiotics, defoliants, and desiccants could also be included.

Pesticides become residues directly or indirectly: (i) by direct application on crops or animals, (ii) plant uptake from treated soil, (iii) drift or runoff from adjacently treated areas, and (iv) by-product contamination, such as residues in meat, milk, and eggs picked up from feeding forage which contained residues. Pesticide molecules are designed to be toxic for effective pest control. Owing to the state of the art of control, and to biochemical similarities in many species, the selectivity of the toxicant is sometimes too broad. Potency occasionally spills over to affect organisms other than the target. Concern for humans and valuable domestic and wildlife species, which may suffer ill effects from long-term exposure, necessitates accurate analysis of toxic residues.

A decade ago the number of pesticides was still comparatively small. Most residue measurements involved either spectrophotometry, combustion analysis, enzymatic methods, or biological assay. However, synthesis of new compounds steadily increased and now we have a veritable arsenal of effective chemicals, with thousands of new compounds being tested each year.

For the kinds of analyses discussed here, the molecular structures of these compounds may be conveniently placed in three broad groups: halogenated compounds, organophosphorus insecticides, and others containing carbon, hydrogen, oxygen, and possibly sulfur or nitrogen. In addition, there are compounds which would fit into two or all of these groups. Prominent classes of compounds include: chlorinated hydrocarbons, organophosphorus esters, phenyl-substituted carbamates and ureas, halogenated phenoxy and benzoic acids, triazines, benzonitriles, nitrophenols, miscellaneous hydrocarbons containing sulfur, and heterocyclic, polynuclear, and organo-metallic compounds.

Residue Sampling, Extraction, and Isolation

A sampling procedure in residue analysis must be designed to minimize not only the errors from biological variability and unevenly distributed spray deposits, but also the extreme dilution errors which are inherent in the procedure. The final measurement is only as valid as the sample is representative.

For example, 1.0 kilogram of an herbicide may be applied to a hectare of soil (the plow layer is estimated to weigh about 0.4 million kilograms) and cultivated in for weed control. When this plot is sampled some time later for residue analysis, 10 to 50 samples may be collected at various stations and depths throughout the field. These samples are sieved, mixed, and subsampled for extraction and analysis. If the final isolated herbicide is contained in 10 milliliters of solvent, and 10 microliters are injected for gas chromatographic analysis, then the fraction of the equivalent total treated soil (0.4×10^6 kilograms) which is represented in the injection is about one part in 10^{11}.

There are numerous problems of residue extraction. Because of the diverse

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