Reports

Lithium-Drifted Germanium Detectors: Applications to Neutron-Activation Analysis

Abstract. *Lithium-drifted germanium detectors for high-resolution gamma-ray spectroscopy reduce the need for wet chemistry in neutron-activation analysis. Problems in fields as diverse as geochemistry and the history of 15th-century printing have proved susceptible to this analytic technique.*

The good energy resolution obtainable with lithium-drifted germanium [Ge(Li)] detectors greatly expands the potential of neutron activation as a quantitative, analytic tool requiring little or no wet chemistry and hence its potential as a tool for nondestructive testing and for measuring elements present in low or trace concentrations. By this method we have analyzed 15th-century printed documents for traces of type metal, mixtures of rare earths, minerals, and air pollutants. We now describe several specific projects to show the advantages and limitations inherent in this analytic technique.

Analyses for type metal on incunabula is illustrative of work now possible with Ge(Li) detectors and not readily possible by wet-chemical or other radiochemical techniques. The history of the technology of movable type has many uncertainties. The metallurgy of movable types before 1540 is largely unknown. While no actual specimens of type from the 15th century are known to exist today, printed documents from this time have survived; that such documents may carry detectable traces of the type in the deposited ink was suggested by Brydges. For an analytic system to be useful in such a search, it must, because of the value of incunabula, be nondestructive in nature. This is readily achieved by neutron-activation analysis.

For exploratory studies, samples of *Civitas Dei* by St. Augustine printed by Sweynheym and Pannartz in Rome, Italy, in 1470 (the *Gutenberg Bible* is dated about 1455), the *Nuremberg Chronicle* printed by A. Koberger, in 1493, and a copper plate engraving taken from the Proceedings of the Royal Society of London, 1775, have been irradiated in the M.I.T. Reactor with a thermal neutron flux of 8×10^{12} n cm^{-2} sec^{-1} (accompanied by 10^8 rad/hr of gamma-radiation) for periods of 10 minutes, 30 minutes, and 8 hours. In these analyses, samples of 3 to 30 cm^2 were cut from printed and blank portions of the documents. Approximately 10 percent of the surface of a printed specimen is covered with ink. No attempts have been made to separate the ink of the document from the paper. Embrittlement of the paper, presumably due to the high gamma-flux in the reactor, results from 8-hour irradiations, but is not noticeable after the shorter irradiations. Gamma-ray spectroscopy with a 6-cm^2 Ge(Li) detector 0.4 cm thick, has been performed from 1 hour to several months after irradiations. Gamma-ray energy resolution is about 5 kev FWHM (full width of the photopeak at half the maximum height of the photopeak).

Activity, soon after irradiation, was predominantly attributable to Na^{24} (half-life, 15 hours) and Cl^{38} (37 minutes). As the contribution from these nuclides decreased, that from others became evident. Nuclides found on a printed portion of a page were also found in comparable abundance in the margin. Approximately 0.5 μg of antimony was found in 30 cm^2 of printed paper taken from the Koberger document. At this concentration, precision, including geometry and counting statistics, is ± 10 percent.

Figure 1 presents a gamma spectrum observed in a sample of the activated Koberger document when a 7.5 by 7.5 cm NaI(Tl) crystal was used. Only the peak resulting from Hg^{203} gamma-ray (279 kev) is readily identifiable; all other peaks are distorted and hence are probably comprised of several gamma-rays having different energies. Figure 2 presents the gamma-ray spectrum observed in the same sample with a Ge(Li) detector. Immediately we can identify several nuclides. The components of the broad peaks observed in the NaI(Tl) data are resolved. Accurate knowledge of each gamma-ray energy and accumulation of sufficient data over time to learn the half-period of each gamma-ray permits identification, with confidence, of most of the decaying nuclides.

The origin of the metals in the paper is uncertain. In samples of printed Koberger paper, a gross-weight ratio of 10 : 1 for tin (observed as Sn^{113}) to antimony was measured. This ratio is not inconsistent with that in an alloy a printer might have used for type metal. The Sweynheym and Pannartz document contained a smaller absolute amount of antimony than the Koberger document.

Analysis for bismuth (via Po^{210} alpha activity) was attempted with a surface-barrier detector made of silicon. After an 8-hour irradiation of the Koberger document, approximately three times more alpha activity was observed on the surface of samples of the printed paper than on samples of the blank paper (2 cm^2 each). This activity, if due to bismuth, indicates 0.3 μg of bismuth on the paper surface. After an 8-hour irradiation of portions of the Sweynheym and Pannartz document, alpha activity above background (about 2 counts per 10^3 minutes) was not observed. Lead, a prime constituent of present-day type, is not readily measurable by activation analysis.

The copper plate engraving from the Proceedings of the Royal Society of London, 1775, contains As (As^{76}) in both printed and blank paper (this was not observed in the early documents), while Au^{198} was found only in the printed paper.

An entire volume, including the binding, of *Cicero's Orations*, printed by Aldus, in Venice, 1519, was irradiated in the M.I.T. low gamma-flux medical facility (neutron flux 2×10^{10} n cm^{-2} sec^{-1}, 10^2 rad/hr of gamma-radiation) for 24 hours. No noticeable embrittlement of the paper occurred. Induced gamma activities demonstrated the presence of most of the elements observed in the Koberger document. Autoradiographs (24 hours each) of individual pages still in the volume are being taken to search out exceptionally radioactive regions which may be indicative of type deposits. Two months after irradiation the book emits 0.5 mrad/hr

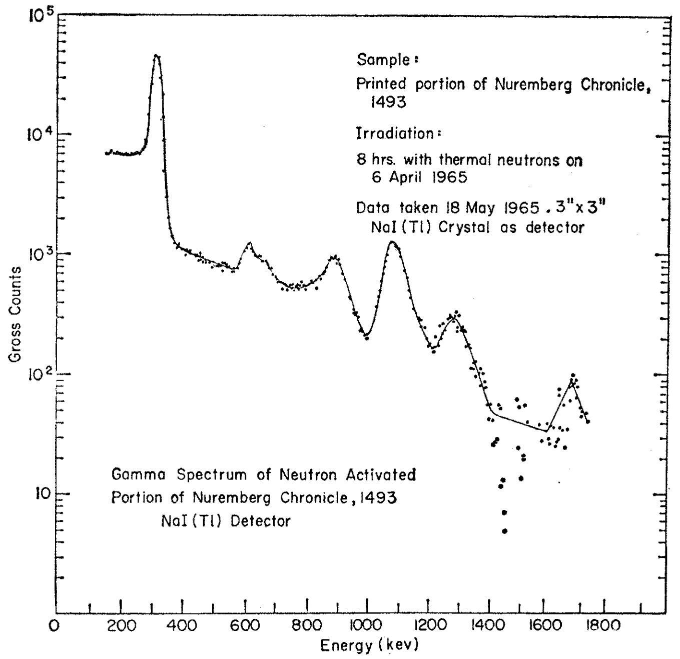

Fig. 1 (left). Gamma-ray spectrum with an NaI(Tl) detector.

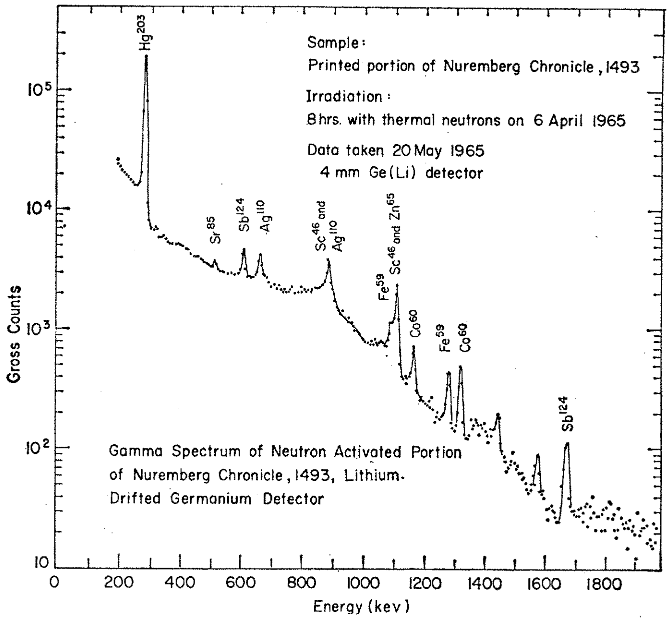

Fig. 2 (right). Gamma-ray spectrum with a lithium-drifted germanium detector.

of gamma-ray dose at contact. It requires no special handling procedures.

The applicability of this tool to chemical analyses of other fragile or valuable samples is clear. The use of the Ge(Li) detector is essential when mixtures of unknown composition are present.

A method of analysis for mixtures of rare earths (the lanthanide series) is desirable. The chemical properties of the elements comprising this group change only slightly with changing atomic number. Because of this, in geologic samples, the systematic variation in the individual rare earth concentration as a function of atomic number is believed to be indicative of the physical conditions that predominated during formation of the sample. The similarity of the chemistry of rare earths makes conventional wet-chemical methods inefficient for quantitative separation of the mixtures.

Gamma-ray spectroscopy of neutron-activated mixtures of rare earths, without chemical separation, permitted quantitative determination of 8 of the 14 naturally occurring elements in this series when all were present in relative abundance similar to that found in basaltic rocks. The measurable elements, La, Ce, Sm, Eu, Tb, Dy, Yb, and Lu, are spread over the series so that the concentration trend of the entire series may be inferred from these data.

Nondestructive whole-rock mineral analysis makes use of the advantages outlined in the previous projects but also points out a serious shortcoming of this technique. In natural samples Na often abounds, and Na^{24}, with its energetic and abundant gamma-rays, is readily produced during neutron irradiation. Hence less abundant gamma-rays from other nuclides are often initially lost in the statistical fluctuation of the Compton contribution from the Na^{24} gamma-rays. This makes difficult the observation of nuclides with half-periods similar to Na^{24}.

Several useful elements are quantitatively detectable, including Fe, Th, and U. The U detection (as Np^{239}) is of interest since U assay is often performed by observing the intensity of radioactivities resulting from the decay of daughter products removed from U by several stages of decay and half-periods of as long as 7.6×10^4 years. The continual chemical processes active in nature make the opportunity for disequilibrium between U and the measured activity great. With U analysis by neutron activation, the intensity of the measured gamma-ray is directly related to the amount of U present.

It is possible to vary the duration of sample irradiation and so preferably augment the activity of one nuclide relative to another. This approach was used to analyze an olivine rock for Ag. An irradiation time of 5 seconds increased the induced Ag^{110} (24 seconds) activity relative to the Na^{24} (15 hours), Mg^{27} (9.7 minutes), and Mn^{56} (2.58 hours) activity. Because of the short half-period of Ag^{110}, counting must be started seconds after the end of sample irradiation. The photopeak of the Ag^{110} 660 kev gamma-ray is located on the Compton edge of gamma-rays from Mg^{27} (843 kev) and Mn^{56} (845 kev). The limit for the detection of a gamma-ray occurs when the number of counts in the photopeak becomes similar to the statistical fluctuation of the background activity in the energy region of interest. For olivine, which is composed of about 50 percent MgO, this limit of Ag detection is about 15 parts of Ag per million (15.5 g of Ag per ton of rock). A syenite rock after a 5-second irradiation would have a background of about one-third of that of olivine in this energy region.

In air pollution studies, elements present in trace or small concentration often may be filtered from the atmosphere, and their abundance on the filter may be directly measured with no wet chemistry before or after irradiation. On a clear day, with winds gusting to 24 km/hr in the vicinity of the air sampling apparatus, the following elements in the stated relative concentrations were collected, by suction, on a $0.5\text{-}\mu$ (pore size) Millipore filter: Na, 100 parts; Br, 24; Zn, 9; Cr, 6; Mn, 1.5; Sb, 1. The absolute Br concentration was about 30×10^{-9} g/m^3 of air. The sample was collected atop a 90-meter building in what was seemingly fresh air. After passage of 5000 liters of air (comparable to 10 hours of human breathing) through the filter, the filter had turned a deep grey with a visibly thick deposit. It is the trace elements, possibly introduced into the atmosphere by only a few specific sources, that may well provide the tag for studying motion and sources of air masses and the more abundant atmosphere pollutants.

Because this analytic technique is basically nonchemical, sample handling is greatly reduced. This decreases the likelihood of sample contamination. The directness of this analytic technique permits confidence limits of the observed data to be estimated accurately from the counting data.

The sensitivity of neutron activation and good resolution gamma-ray spectroscopy for determining, in mixtures of elements, the abundance of even those elements present in trace concentrations immediately makes evident further applications of this tool in fields seemingly far removed from gamma-ray spectroscopy.

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Notes

1. Supported in part by the U.S. Atomic Energy Commission under contract AT(30-1)-952. The type metal work is being performed in close collaboration with C. S. Smith, Humanities Department, Massachusetts Institute of Technology. The rare earth mixtures were obtained from J.-G. Schilling, Department of Geology, M.I.T.

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Rubidium-Strontium Age of the Bosumtwi Crater Area, Ghana, Compared with the Age of the Ivory Coast Tektites

Abstract. *Rocks from the vicinity of Bosumtwi crater, Ghana, and a representative collection of Ivory Coast tektites have been analyzed mass spectrometrically for rubidium, strontium, and strontium isotopic composition. The data from the rocks of the crater area yield an age of 1.97* $\times 10^9$ *years* ($\lambda_{Rb} = 1.47 \times 10^{-11}$ *year*$^{-1}$)*. The data for the Ivory Coast tektites fall on this isochron. This identity of age values for the Ivory Coast tektites and the Birrimian basement rocks of West Africa strongly supports the hypothesis of terrestrial formation for these tektites. The evidence available at present suggests that the Ivory Coast tektites are most probably the fusion products of meteoritic impact at the Bosumtwi crater site.*

The purpose of this study was (i) to determine if the Ivory Coast tektites fall on the 400-million-year isochron which has been suggested (*1*) for tektites from the other three major geographic localities, namely, Australasia, Czechoslovakia, and North America; and (ii) to compare the rubidium, strontium, and strontium isotopic compositions of the Ivory Coast tektites with those of the rocks at the Bosumtwi crater in Ghana. Maclaren (*2*) first suggested, in 1931, that the Bosumtwi, or Ashanti, crater was formed by meteoritic impact. The discoveries of coesite (*3*) and shatter cones (*4*) at the crater support this theory. Cohen (*5*) suggested that the Ivory Coast tektites, which occur approximately 300 km to the west of the crater, might have been produced by the impact. Since then, K-Ar analyses of Ivory Coast tektites (*6*) and Bosumtwi glass (*7*) have yielded the same age, within rather large experimental uncertainty, of 1.3 (± 0.3) $\times 10^6$ years. Recently, fission track dating (*8*) has supported this agreement between the time of melting of the crater glass and the Ivory Coast tektites.

All but two of the tektites analyzed, GSFC Nos. 3 and 4, were from a group of 75 samples recently obtained from the Ivory Coast. Details of this collection, such as specimen locality, weight, density, and so forth, are in preparation for later publication. The samples analyzed were chosen to cover the specific gravity range of the collection and to cover the range of Rb/Sr ratios, which were estimated from rough x-ray fluorescence measurements. All of the tektites, except GSFC No. 4, are from the approximately 45- by 80-km strewn-field area described by Lacroix (*9*). Tektite GSFC No. 4 was found in 1963 in a prospecting pit 2 km south of Adzopé; this is approximately 100 km to the south of the previously defined strewn-field.

The rubidium, strontium, and strontium isotopic compositions for the tektites are given in Table 1; those for the rocks of the Bosumtwi crater area, in Table 2. The rubidium and strontium determinations are by stable isotope dilution techniques, while the isotope ratio analyses are on unspiked strontium. The basic analytical procedures have been previously described (*1*). Precision of the rubidium and strontium isotope dilution analyses, as demonstrated by replicate analyses, is approximately ± 2 percent. The strontium isotopic ratios reported in Tables 1 and 2 were determined on four different mass spectrometers of similar design (12-inch radius of curvature, 60° sector, single focusing) at the Massachusetts Institute of Technology, the Goddard Space Flight Center, and the National Bureau of Standards. Most of the samples were analyzed on at least two of the machines; only the average values for each sample are reported in the tables. No systematic bias was observed between the machines; the average difference between $(Sr^{87}/Sr^{86})_N$ analyzed on the same sample was less than 0.1 percent for samples analyzed repeatedly on the same mass spectrometer and for samples analyzed on different machines.

The tektites in Table 1 are listed in order of increasing specific gravity. Thus they are probably listed in approximate order of decreasing SiO_2 content, as the inverse correlation between specific gravity and SiO_2 content has been demonstrated in several studies (*10*). The data in Table 1 suggest an inverse correlation between specific gravity and rubidium, but no correlation is evident between specific gravity and strontium.

The Ivory Coast tektites exhibit a rather restricted range in both rubidium and strontium, as has been observed for most elements in tektites. The strontium content in GSFC No. 4, however, is far outside the range of the other 12 samples. This value has been checked by two independent analyses, which agreed within ± 1 percent. The values for rubidium and strontium in Table 1 are in excellent agreement with the single reported analyses in an Ivory Coast tektite of 64 ppm Rb and 316 ppm Sr (by x-ray flourescence techniques) by Gentner *et al.* (*7*). They also report rubidium and strontium in a Bosumtwi glass from the same