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NON-DESTRUCTIVE DETERMINATION OF TRACE-ELEMENT CONCENTRATIONS

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SUMMARY

A beam port has been installed at the National Bureau of Standards (NBS) reactor by the University of Maryland group in co-operation with the NBS staff in order to initiate studies of a new analytical technique: neutron-capture prompt γ -ray activation analysis (PGAA). A detection system based on a large, high resolution Ge(Li) detector surrounded by a NaI crystal has been developed for measurement of prompt γ rays from 80 keV to 11 MeV. With a temporary external beam tube in place, neutron and γ -ray backgrounds were investigated prior to design and construction of a well-shielded beam tube and massive shielding for the detection system. With the backgrounds suitably low, it has been possible to investigate γ -ray spectra of a wide range of samples. These spectra are being carefully analyzed to identify species contributing the observed lines. Whenever an element's presence is suspected, standards of the pure element or simple compounds are irradiated to determine its complete spectrum. This is necessary in order to determine which lines are useful for analytical purposes and which have interferences from other elements. From the results to date, it appears that PGAA will be able to measure the following elements in many types of samples: H, B, C, N, Na, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Cd, Sm and Gd. Many other elements will be measurable in certain classes of samples. Furthermore, the list of elements is incomplete, as not all lines have yet been identified in the spectra. The quantitative application of the method is being tested using a wide range of NBS Standard Reference Materials whose elemental compositions are well characterized. Measurements are reported for about fourteen elements in several standards. In general, the agreement with previous measurements is quite good.

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I. INTRODUCTION

There are many areas of research and development in which there is a constant need for improved methods of elemental analysis applicable to a wide range of types of samples. This is especially true of the energy industry in which detailed analyses of geochemical samples are needed in the search for fuel deposits, of coals, oils and oil shales for the design of conversion processes, of the effluent streams from existing plants or prototypes for control of environmental problems, of high-purity materials for use in solar cells, just to mention a few obvious examples. Improved elemental analyses are also needed for many other purposes, e.g., in the search for mineral resources, in studies of diseases related to trace metal excesses or deficiencies, in investigation of limits of soil fertility imposed by trace element availability, etc.

Over the past ten years, our group and others have developed powerful instrumental methods, especially instrumental neutron and photon activation analysis (INAA and IPAA, respectively) by which one can measure concentrations of a wide range of elements in materials such as coal, soil, oil, atmospheric particulate material, sediments, natural waters, rain, etc. (1-3). These methods have many advantages relative to competing techniques in that they can be used to measure a very large number of elements reliably in the same sample without the necessity of dissolving the samples, thus avoiding problems of the loss of insoluble materials, contamination of solutions by reagents, etc. Instrumental nuclear methods have the advantage, relative to other non-destructive methods, especially x-ray fluorescence, that both the projectiles (e.g., thermal neutrons, high energy photons) and the emitted γ rays have such long ranges in materials that self-absorption is rarely significant.

Despite the many advantages of "off-line" nuclear methods (i.e., those such as INAA and IPAA in which one observes decay of radioactive products after irradiations), they have some limitations, especially: (1) their inability to measure some important elements in most matrices of interest; (2) the long turn-around time for complete analyses in order to observe long-lived products; and (3) the limits of size and safety of samples that can be injected into reactors.

To avoid these limitations of off-line nuclear methods, while still exploiting their advantages, we have been working on the development of an on-line method, neutron-capture, prompt γ -ray activation analysis (PGAA). According to this method, one observes the prompt γ rays emitted almost immediately (usually $<10^{-14}$ sec) after each neutron capture. It was expected and we have now shown, that one can observe a number of elements via prompt γ rays that do not have suitable radioactive products for off-line observation. Furthermore, the method can have very fast turn-around time, as all of the data are available at the end of the irradiations. Furthermore, if the PGAA is done using an external neutron beam (as we are doing), the method is almost non-destructive as the flux is quite low and samples are subjected to no heating. Also, one could irradiate samples that are too large, dangerous or fragile to be placed inside a reactor.

Prompt γ -ray activation analysis has been under consideration for more than ten years and several papers on the subject have appeared in the literature, e.g., Refs. 4-7. However, the method has not been fully developed and exploited. In the published works, the authors have done calculations that demonstrate the potential of the method or they have demonstrated the sensitivity of the method by irradiation of pure elements or by measuring concentrations of a few elements with strong prompt γ -rays in several samples. However,

these limited studies have not been sufficient to exploit the full potential of the method and investigate it thoroughly enough that it can be used in a fairly routine way. In order to do that, one needs to irradiate a wide range of materials, collect the data with a detection system of the best possible resolution and efficiency from about 100 keV to 11 MeV, identify all obvious lines in the spectra, take careful spectra of pure elements or simple compounds of each element whose lines are observed in the spectra, determine interferences between γ rays of different species and, from all of this, decide which lines can be safely used for the analysis for each of the observed elements. Our objective in this study is to perform these detailed, careful measurements that must be done if the method is to be made useful. For the most part, capture γ -ray spectra of the elements are not well enough known to determine the capabilities of the method by calculations. In fact, we have been somewhat surprised at the poor quality of much of the existing data in this field. In some compilations, the energies of lines are wrong by several keV and there is little assurance that all of the lines listed really belong to the element rather than to impurities in the elemental standard.

As described in more detail in last year's Progress Report (ORO-5713-001), we have set out to build a system with a high quality external beam from the National Bureau of Standard's (NBS) reactor coupled with a sophisticated counting and data handling system for taking spectra of high resolution up to 11 MeV. At the time of writing last year's Progress Report, we had constructed the parts of the lower beam tube, had received the main portion of the analyzer system, and had ordered the NaI anti-Compton shield detector.

During the past year, the following steps have been taken:

1. The lower beam tube was put together and inserted into the reactor.
2. The original upper beam tube (external to the reactor), target holder and beam stop were assembled and put in place.
3. Measurements of the quality of the beam and the backgrounds of scattered neutrons and γ rays were made.
4. On the basis of #3, a new upper beam tube was built with better shielding to lower the backgrounds.
5. The large Ge(Li) detector, the NaI crystal surrounding it and the associated electronics were obtained and installed. A large shield was built to surround the entire detector set-up.
6. The multi-channel analyzer system was debugged and now runs quite well.
7. We are now taking spectra of a wide range of samples and elemental standards, analyzing them in terms of the elements observable, and testing the quantitative application of the method.

As described in more detail below, the results obtained to date are very encouraging. Already we have observed lines of 20 elements in the spectrum of NBS Fly Ash (SRM 1633A), the most thoroughly analyzed spectrum to date, and there are still many lines not identified. Of these elements, many are measured with great difficulty, if at all by INAA: H, B, N, Si, P, Cd, Gd and Dy.

II. EQUIPMENT AND METHODS

A. Lower Beam Tube

The lower beam tube, whose design and construction were described in detail in last year's Progress Report, was assembled and inserted into the reactor in September 1977. The upper beam tube (described below) and the beam stop were quickly put in place above the port and measurements of the beam were made. Radioautographs of the neutron beam showed that the useful beam diameter is about 4.5 cm at the sample location, about 1 m above the top of the reactor. The neutron flux is constant to within 5% and, across the central 3 cm, it is constant to within 3% (see Fig. 1). Gold foil, with and without Cd covers, yielded a gold-cadmium ratio for the thermal/fast neutron flux of 55/1 as had been predicted on the basis of the location of the lower end of the beam tube in the D_2O reflector region just outside of the core. The gold foils were also used to determine the neutron flux as 2×10^8 n/cm²-sec, with an integrated flux of 3×10^9 n/sec over the beam. Note that the flux is within 10% of the original design figure of 2.2×10^8 .

B. Upper Beam Tube

The original upper beam tube was a 4-in. Al pipe with a cyclotron "slit box" serving as the target holder. This set-up was intended to be temporary, i.e., just a simple set-up that would allow us to check backgrounds under various conditions. And with that set-up, the backgrounds were indeed quite large. Only a very small fraction of the beam scattered out to the vicinity of the detector, but a small fraction of 2×10^8 n/cm²-sec is still a very large background! We were concerned not only with neutron and γ -ray backgrounds during experiments, but also about permanent damage to the Ge(Li) and NaI crystals caused

Fig 1. Radioautograph of beam obtained by activation of a thin layer of Dy, placing the activated sample against a film developing the film and making a densitometer trace of the film.

by capture of neutrons in the detectors, making them radioactive, and deterioration due to radiation damage.

By using the temporary system, we could easily check the effects of various shielding and neutron-absorber configurations. We quickly found that the considerable neutron scattering by air molecules in the beam tube could be greatly reduced by purging the tube with He (at 1 atm), which has a much smaller scattering cross-section. Also, we found that the diameter of the beam tube was too small, allowing neutrons in the fringe of the beam to strike it and scatter.

On the basis of the above experience, a new beam tube was designed and built. This beam tube (see Fig. 2) consists of three concentric tubes of Plexiglass, which is less massive and expensive than Al. The diameter of the inner tube was increased to 6 in. to reduce impingement of the fringe of the beam on the walls. The space between the inner tube and the next one out (10-in. diam.) is filled with paraffin so that both the paraffin and the Plexiglass thermalize the scattered neutrons. Between the second and third tubes is a 0.75-in. thick layer of boron carbide (B_4C) in a paraffin matrix. Polycarbonate polymer or 1-mil Teflon films are now used as end windows of the beam tube. Note that they do not have to support a large pressure differential, as He is maintained at 1 atm inside.

A Plexiglass sample box was placed at about 110 cm above the floor to line up the target with the detector system described below. It was surrounded by plates of B_4C in polystyrene to absorb neutrons scattered by the sample. An Al support tower was constructed to hold the entire upper beam tube assembly in place and allow for careful alignment of it.

Fig. 2 Beam Tube and Detector System

It is essential that the mass of anything placed in or near the beam other than the sample be as small as possible to avoid neutron and γ scattering and neutron capture that would yield background in the prompt spectra. Thus, to position samples in the beam, we've been sealing them in 1-mil Teflon film and suspending the film in the beam with thin fish line.

Preliminary tests with this new design showed that it indeed reduced neutron and γ -ray backgrounds by a factor of about 10^3 along most of the beam-tube length. These measures, coupled with the shielding of the detector system itself (discussed below), have reduced backgrounds to acceptable levels, both from the point of view of interference with sample spectra and of long-term damage to the detectors.

C. Detector Shield

The detection system consists of a 24% efficient (relative to an 7.6- x 7.6-cm NaI crystal), true coaxial Ge(Li) detector surrounded by a cylindrical 30- x 38-cm NaI crystal which is separated symmetrically into two independent halves for observing 511-511 keV coincidences. The NaI crystal is operated in anti-coincidence with the Ge(Li) detector to obtain "Compton-suppressed" spectra from the latter and, simultaneously, in triple coincidence with the Ge(Li) detector. In the latter mode, one obtains "pair" spectra, i.e., the spectrum of annihilation-photon double-escape peaks by requiring a triple coincidence between a 511-keV photon in each half of the NaI detector and the double-escape event in the Ge(Li) detector.

Even in a normal counting room of reasonably low background, a Compton-suppressed detection system must be carefully shielded. The large NaI crystal has such a large counting efficiency that even a

normal background produces such a high count rate that it keeps the system "dead" much of the time when operating in the anti-coincidence mode with the central detector. The importance of good shielding is, of course, much greater in our situation, where one has elevated backgrounds. Thus, we have built a massive shield to reduce the γ -ray background to acceptable levels and to provide additional protection against neutron capture and radiation damage.

A diagram of the detection system and shielding is shown from different perspectives in Figs. 2 and 3. A cylinder of Pb of about 5-cm thickness surrounds most of the NaI crystal. This is surrounded by three, concentric Al cylinders. Between the inner and middle Al cylinders is additional Pb of about 5 cm thickness. The space between the middle and outer Al cylinders is filled with B_4C in polystyrene to stop any neutrons heading towards the detectors, especially from the beam stop above the beam tube. The ends of the cylinder are covered with caps consisting of Pb and B_4C in polystyrene except for the entrance port for the Ge(Li) detector and the collimator of γ rays from the target. Note that it is necessary to have Pb shielding between the B_4C and the detectors to cut out the 477-keV line from neutron captures in boron. It would be preferable to absorb neutrons in 6Li , but that is prohibitively expensive in the amounts that would be required to surround the whole beam tube and detection system.

A Pb collimator, 15-cm long with a 2.5-cm I.D. is placed between the sample position and the Ge(Li) detector. A 2.5-cm long, fused 6Li_2CO_3 plug is placed inside the collimator to prevent neutrons scattered by the sample from striking the detector. Of course, this plug causes some attenuation of low-energy γ rays and tests are now being made on the effectiveness of the plug. If it's not needed, it

Figure 3 Detection System and Shielding Configuration

will be removed to allow for better detection of low energy γ rays.

D. Backgrounds

The shielding configuration appears to be quite effective. The neutron flux at the outside of the detector shield is about $30 \text{ n/cm}^2\text{-sec}$ and essentially zero at the Ge(Li) detector. We have taken background counts with no sample (but the sample holder) in place. As shown in Table 1, the major background lines are from neutron capture in H, B, N, C, Fe and Pb. The capture in H and C probably occurs in the Plexiglass beam tubes and that in B in the B_4C around the sample box. Capture lines of Pb and Fe and the decay line of ^{28}Al are from construction and shielding materials. The N capture probably occurs both in the air near the sample box on the side opposite the detector and in the liquid nitrogen Dewar beneath the Ge(Li) detector. If the latter is the major source, we can add some shielding to reduce it. A small background peak at 1294 keV is due to ^{41}Ar in the air. There are also background lines from ^{60}Co decay. Weak lines of fluorine are observed with the Teflon film used for packaging of samples in the beam. Very weak lines of Ge and I are observed in several-hour counts of samples due to neutron capture in Ge and I of the Ge(Li) and NaI detectors themselves (see Fig. 5). They are much reduced when taking backgrounds with nothing in the sample holder or just a Teflon film. Apparently, they arise mainly as a result of neutrons scattered off of more massive targets in the beam.

Although further reductions of background lines may be possible, they are probably acceptable for most purposes. Even in the presence of the H and N background lines, we estimate that these elements can be measured accurately in samples having concentrations greater than about 0.5%. In Table 1 we compare count rates of background lines with

Table 1. Comparison of Background Lines with and without Sample of NBS Standard Oyster in Position^a

E _γ (keV)	Source Element	Peak area count rate (c/sec)	
		Oyster ^a	Background ^b
477	B	4.65 ±0.1	0.484 ±0.02
511	β ⁺ annihilation	3.80 ±0.02	1.96 ±0.01
1173	⁶⁰ Co decay	0.086 ±0.008	0.070 ±0.004
1294	⁴¹ Ar decay	0.052 ±0.008	0.017 ±0.004
1333	⁶⁰ Co decay	0.043 ±0.008	0.091 ±0.004
1779	²⁸ Al decay	0.083 ±0.010	0.006 ±0.003
1885	N	0.22 ±0.01	0.077 ±0.003
2223	H	51.8 ±0.1	1.85 ±0.01
2521	N	0.043 ±0.005	0.016 ±0.002
3532	N	0.048 ±0.003	0.024 ±0.001
3678	N	0.076 ±0.004	0.026 ±0.002
4945	C	0.169 ±0.005	0.006 ±0.001
5269	N	0.131 ±0.005	0.045 ±0.002
5533	N	0.074 ±0.004	0.027 ±0.002
5562	N	0.047 ±0.004	0.014 ±0.001
6322	N	0.061 ±0.004	0.020 ±0.001
7299	N	0.021 ±0.002	0.005 ±0.001
7368	Pb	0.031 ±0.002 ^c	0.0032±0.0006
7632	Fe	0.0037±0.0014	0.0051±0.0006
7646	Fe	0.0067±0.0014	0.0042±0.0005
10830	N	0.015 ±0.001	0.0054±0.0004

^aMass of oyster sample 1.12g. Background was taken without Teflon film.

^bErrors are only statistical uncertainties in net peak-area. Some of these are very small peaks in the fly ash spectrum, so actual errors are much greater.

^cPossibly due to interference by another element.

those of the same lines with an oyster in place. Since there is very little Fe in the oyster, we see essentially the background values. By contrast, the Fe lines have count rates of about 0.3/sec in the fly ash spectrum (see Sect. III. B.),

E. Detection System

The detection system, described briefly in Sect. I.C., is sketched in Fig. 3 and the electronics are outlined in Fig. 4. Most of our work to date has been with singles spectra from the Ge(Li) detector, with the region from 0 to 4 MeV obtained from an ordinary amplifier and stored in 8,192 channels of the memory and the region from about 3.2 MeV to 11 MeV obtained from a biased amplifier and stored in a second group of 8192 channels. Selected portions of the capture spectrum of NBS Fly Ash are shown below in Fig. 5.

The split NaI crystal is present for use in obtaining Compton-suppressed and pair spectra. In the Compton-suppressed mode, all γ -ray events occurring in the Ge(Li) detector which have coincident events in either half of the NaI crystal (within about 50 nsec) are rejected by the multi-channel analyzer to eliminate most events in which a Compton scattering in the Ge(Li) is followed by escape of the scattered γ ray. This will reduce the general Compton background in spectra, allowing us to observe weak lines with greater sensitivity. At present the system has been tuned to give a background reduction of factors of three to five, depending on the energy region. We expect that further tuning of timing circuits, pulse shapes, etc. will yield a further background reduction by a factor of three or more. We have started taking some prompt spectra with Compton suppression and will do so routinely as soon as the optimum settings are made.

Preliminary work on the set-up for taking pair spectra has begun

Fig. 4. Schematic diagram of electronics used for obtaining singles spectra from 0 to 4 MeV and 4 to 11 MeV with regular and biased amplifiers, respectively, and, simultaneously, Compton-suppressed and pair spectra.

and should be completed during August, 1978. In this mode, the analyzer accepts only those Ge(Li) signals that are in coincidence with 511-keV annihilation photons in both halves of the NaI crystal. The resulting spectrum that is stored will contain only double-escape peaks, at the γ -ray energy minus 1022 keV. This should be very useful, as the spectra of complex samples contain a very high density of lines, with much overlap. In the "singles" spectrum, one observes three peaks for each γ ray: the full energy peak (E_γ), the single-escape peak (at $E_\gamma - 511$ keV) and the double-escape peak (at $E_\gamma - 1022$ keV). The pair spectrum will retain only the last of these, thus reducing the complexity of the spectrum three-fold without any loss of information.

F. Data Handling

Data from the three counting modes will be simultaneously stored in the Tennecomp TP-5000 analyzer system whose central component is a PDP-11/34 computer with a 128K-word core, of which 28K is available for software, 4K is hard-wired for peripherals, and 48K is for data accumulation. The remaining 48K is unavailable at present, but will become available when Tennecomp delivers their long-awaited TPOS II system program. The system has inputs from six 8,192-channel analog-to-digital convertors (ADCs). We have been using two ADCs for singles spectra, one with input from an ordinary amplifier from 0 to 4 MeV and the second with input from a biased amplifier covering the region from 3.2 to 11 MeV (see Fig. 4). The remaining ADCs and storage will be used for accumulating Compton-suppressed and pair spectra and, possibly, for singles spectra from a second Ge(Li) detector of high geometry (discussed in the present proposal). Data may be viewed during experiments on a 10-in. scope. At the conclusion of an experiment, the data are stored on magnetic disks and/or tapes.

Once an experiment has been set up and data are being accumulated, the computer can be used to reduce data from previous experiments that are read in from disk or tape. A program is now available to calculate an energy-vs-channel number equation from the locations of standard peaks in the spectrum. Once the energy scale is calibrated, we use a rather simple search-and-fit routine to locate peaks and determine their net peak areas and energies. The program searches for significant changes of slope in the spectrum and, when found, searches for the peak channel. It determines the energy corresponding to the peak channel and calculates the net peak area after subtraction of a straight-line background. Following treatment of a spectrum, we obtain a print-out that lists each peak found, its maximum channel number (an integer) and the corresponding energy, the net peak area and the magnitude of background subtracted, along with the uncertainty of the peak area as determined from Poisson statistics. (For obtaining precise positions of peak maxima, we also have a program that computes peak centroids in fractional channel numbers.) This program, although greatly reducing our hand calculations, is not entirely satisfactory, as it misses some small, but clear peaks observable in plots of the spectra and does not resolve close-lying doublets well. We are now writing an improved search-and-fit routine that will be similar to those described by Op de Beeck (8). This routine should retain the speed and simplicity of our present method, but improve efficiency considerably.

Programs of the type described above are needed now, as we are in the process of identifying all of the lines in spectra from various samples. But when this job is complete and we know which lines to use for analysis for each element, a different approach will be needed

for routine analytical use. In that case, we will need a program that has built into it the appropriate lines to use for each element. In order to prepare for that, we have developed a similar program for analysis of spectra taken at short times after neutron activation of samples (9). It searches only for peaks that are known to be emitted by short-lived irradiation products of elements normally observable in a wide range of types of samples. It uses the area of these peaks, along with those of the same peaks in the spectra of monitors containing known amounts of the elements to calculate the mass of each element in the sample and its uncertainty, making corrections for decay between counts, decay during counts, dead time and flux. For those peaks that contain interferences, it also calculates the magnitude of the interference and subtracts it. If desired, this program displays the fit to each peak on the scope and allows the user to modify the fit (e.g., the assumed background) by use of a light pen. A similar program will be developed for prompt γ -ray spectra as soon as we have identified the best lines for analytical use and any interferences that must be removed.

III. RESULTS

A. Introduction

Using the system as described above, we have begun to develop the analytical applications of PGAA by irradiating a wide variety of samples of various types, most of them NBS Standard Reference Materials (SRMs), which are rather well characterized, so that we can check the quantitative application of PGAA for as many elements as possible. At present we have irradiated existing SRMs for coal, fly ash, orchard leaves, bovine liver, plus several new materials under development as SRMs, eastern and western coal, a new fly ash standard, river sediment and

oyster. We have also irradiated a biological material under investigation in another of our projects, freeze-dried human saliva (10), and samples of ores from a copper smelter.

As shown in the examples below, these spectra are enormously complex. We have been using existing compilations of prompt γ -ray spectra (11-13) to identify the lines as far as possible. For each element whose lines are identified, we prepare a pure elemental standard, if possible, or a simple compound of it for irradiation, in order to determine the complete prompt γ -ray spectrum for the element. It is necessary to do this, as we have found that most compilations of prompt γ -ray spectra are inadequate as, energies of lines at high energies are often incorrect by several keV, some weak lines have been missed and we find that some lines listed for specific elements are, in fact, associated with impurities in the elemental standards. It is essential that one know the energies and relative intensities of all spectral features produced by an elements, as the spectra are so complex that even very weak lines of an element with a large cross section could give a substantial contribution under lines of the same energies belonging to other elements. For quantitative analytical purposes, it is essential to know either that the peaks used for the determination are "clean", or to know the identity of the interferences and the magnitudes of corrections for them.

Before running other samples, it was necessary to find a packaging material for samples that would cause minimum interference with the sample spectra. Fully deuterated polyethylene would probably be ideal, but we've been unable to locate supplies of it. Ordinary polyethylene produces an enormous H capture line (at 2223 keV) and would make it impossible to measure H concentrations in samples.

In the amounts needed for strength, graphite is too massive, causing excessive neutron scattering. Teflon films are the best choice we've found, as fluorine has such a small cross section that it produces only very weak background lines. Because of its small cross section, it probably wouldn't be possible to measure F in most samples, anyway, so this choice does not require sacrifice of a measurable element.

B. Treatment of the Spectrum of NBS Fly Ash

We can best illustrate the process that we have to go through to develop this analytical procedure for a particular class of samples by considering the example of NBS Fly Ash (SRM #1633A). We have studied this sample the most thoroughly because its matrix is rather like that of many crustal samples, but the concentrations of many trace and minor elements are enriched with respect to the crust, giving us a better chance to observe them than in soil or rocks. Portions of the spectrum of NBS Fly Ash are shown in Fig. 5, with assignments of all peaks thus far identified. We have not shown the complete spectrum as it covers 16,384 channels! The steps that we go through to analyze such a spectrum are as follows:

1. Computer reduction of spectrum. The entire spectrum is run through the program discussed in Sect. II.F. to obtain approximate energies and count rates under each peak.
2. Comparison of Energies with Prompt γ -Ray Compilation. Starting with the strongest peaks in the spectrum, we identify the lines by comparison of energies with the prompt γ -ray compilations (11-13). Especially at high energies, the agreement between energies from the computer output and those listed in compilations are not very good, partly because our initial calibrations were not very accurate and partly due to the fact that energies given in the compilations are frequently off by several keV. As discussed in Sect. III.D.,

Figure 5. Selected regions of the prompt γ -ray spectrum observed by irradiation of 0.82-g sample of NBS Fly Ash (SRM 1633A) for 20 hrs. Portions 1, 2 and 3 were obtained with the regular amplifier and portions 4 and 5 with a biased amplifier. Peaks are labelled by the energy of the peak in keV and the element of origin, where identified. Many small, unlabelled peaks at low energy are known to be from Gd and/or Sm. Energies are based on our own calibration lines (see Sect. III.D.) and should be accurate to ± 0.2 keV.

1. Region from 70 to 520 keV.
2. Region from 515 to 880 keV.
3. Region from 880 to 1390 keV.
4. Region from 5800 to 6720 keV.
5. Region from 6720 to 7700 keV.

we have now determined energies for some calibration lines up to 10.8 MeV to an accuracy of about 0.3 keV, so we will be able to determine energies of most peaks to about ± 0.5 keV or better. When an element appears to be present, we check the spectrum for the presence of all of its reported lines, including the escape peaks of all high energy lines.

3. Quantitative Spectral Check. Once we suspect that lines of an element are present, we run a sample of the pure element or a simple compound. The results of the computer analysis of the spectra of the sample and the elemental standard are compared by normalizing the count rate under each peak to one of the most intense peaks for the element. These normalized rates are then compared by dividing the fly ash by the results from the elemental standard. If the resultant ratio is unity, then the peak in the fly ash spectrum is probably all from the element in question. If substantially less than unity, then it probably contains major contributions from some other element. A check of several Si lines in the fly ash spectrum is given in Table 2. From the results in Table 2, it appears that the peaks at 1273, 3539, 3912 and 4423 keV in the Fly Ash spectrum are entirely due to Si prompt γ rays, whereas those at 3055, 3678 and 5358 keV have appreciable contributions from other lines. At high energies, one must also account for the single- and double-escape peaks (SE and DE) relative to the full-energy peak (FE). As shown in Fig. 6, we have constructed a calibration curve that can be used to calculate SE and DE peak intensities from that of an FE peak. As shown in Fig. 5-2, the peak at 752 keV has

interference from a peak at 749 keV (now known to be Sm and Gd). The line at 3054 keV contains interference from Mg.

Table 2. Comparison of Count Rates of Several Peaks in Spectra of Irradiated Fly Ash and Silicon Standard

E _γ (keV)	Count rate (norm. to 3539-keV line)		Ratio Fly Ash/Std.	% of Peak from Si
	Si Std.	Fly Ash		
752.2	0.0825	0.104	1.25	80
1273.3	0.566	0.510	0.90	111
1446.1	0.0167	0.0171	1.02	98
3054.5	0.0128	0.0442	3.46	29
3538.6	<u>1.00</u>	<u>1.00</u>	<u>1.00</u>	<u>100</u>
3677.7	0.0074	0.034	4.65	22
3911.6	0.225	0.218	0.97	104
4423.0	0.368	0.376	1.02	98
5358.2	0.039	0.057	1.46	68

Figure 5 clearly demonstrates that prompt γ-ray spectra are very complex, especially between 500 and 1400 keV. Lines from Gd and Sm are so numerous that they interfere with peaks of many elements. The spectrum of fly ash becomes much less complex at higher energies, but as shown in Figs. 5-4 and 5-5, some interferences occur even there. Although not shown here, we've found that marine and biological samples contain an enormous number of lines from Cl, even at high energies, that interfere with or completely obscure some of the lines observed in fly ash. However, spectra of biological samples contain very little Sm and Gd interference.

These spectra illustrate the necessity for running standards of each element whose lines are suspected in the spectrum. Only with the use of standards can one determine these interferences and, thus, identify clean lines for analyses. In some cases, no completely clean lines are available for some elements, but one can still use

Fig. 6. Ratios of areas under peaks resulting from single- and double-escapes of annihilation photons and full energy peak areas.

contaminated peaks by determining interference contributions with the elemental standards.

It is not sufficient to use a single standard of each element. No elemental standard is completely pure. Some elements such as Cd, Gd and Sm have such large cross section that, even if present in other elemental standards at minute levels their lines appear. For example, in Rasmussen's compilation (11), a γ ray at about 560 keV is listed for many elements. We see that line in some of our standards, too, and suspect that, in many cases, it comes from Cd contamination of the standards. Likewise, we've seen lines of Gd and Sm in various of our standards. It is not clear in the compilations of prompt γ -ray spectra if the studies quoted have taken care to remove impurity lines from their γ -ray lists. Probably the best way in which to check this is to run several standards for element, using materials from different sources. Presumably, the levels of impurities will differ from one source to another, a change which would be reflected by variable relative intensities for impurity lines or complete absence of the lines for some highly pure standards. We will run several different standards for each element, but haven't had a chance to do so yet.

So far, in the fly ash standard, we have identified measurable peaks for 15 elements as listed in Table 3. We have listed only those elements whose lines appear to be present above background levels, e.g., not C and N, whose lines are at above background levels. Elements in this list have been quantitatively identified, meaning that the procedure described above has been carried out. Lines for some other elements have been tentatively assigned in the spectra of Fig. 5. In addition to the list of Table 3, tentative identifications of lines

Table 3. Elements Identified in NBS Fly Ash Spectrum

Element	Energies of Prominent γ -Rays (keV) (full-energy peaks only) ^a
H	2223
B	477 (v. short lived, Doppler broadened)
Na	1369D, 2754D
Mg	2831, 3054, 3413
Al	1526, 1778D, 2283, 2960, 3465, 4691, 4734, 7725
Si	1273, 2426, 3539, 4423, 4934, 6380
K	770, 1304, 1619, 2047, 5752, 7259
Ca	520, 1942, 3609
Ti	342, 1382, 1499, 1586, 1762, 6761, etc.
V	646, 1434D
Mn	847D
Fe	352, 692, 1019, 1725, 7632, 7646
Cd	558, 651
Sm	334, 439, 584, 712, 737, 1186, etc.
Gd	181, 199, 780, 944, 962, 977, 1108, 1119, 1187

^aD indicates line is from radioactive decay of capture product. Inclusion in this list does not mean that a line is "clean", but rather, that the element makes a substantial contribution to the line in question, whose total strength has been approximately accounted for.

of Dy, S, P and Cl have been made. Some of the lines in Table 3 have been used for quantitative determinations of elemental concentrations in the fly ash, as described below in Sect. III. E. The same kind of study of the spectra of other irradiated samples is also in progress.

C. Summary of Spectral Identifications

In addition to the NBS Fly Ash, (SRM 1633A), we have irradiated the following samples:

1. NBS SRM 1632 Coal Standard - well characterized by NBS and many other groups (e.g., Ref. 14) for over 40 elements. Unfortunately, the standard has been so popular that the NBS supply is exhausted. In its place, NBS has issued two new coal standards, see #2 and #3.
2. NBS SRM 1632A Coal Standard - (Bituminous, Eastern Coal). NBS recently certified for 14 elements and gave "information values" for 12 more. Several people in our group have been measuring as many elements as possible by INAA and other methods in this and SRM 1635 (see #3). We are drafting a paper (similar to Ref. 14) in which we will give values for 40 or more elements in 1632A and 1635. We hope to include data from PGAA in that paper along with values from other nuclear methods.
3. NBS SRM 1635 Coal Standard - (Subbituminous, Western Coal). NBS recently certified for 14 elements and gave "information values" for 12 more. See comment for #2.
4. NBS SRM 1633 Fly Ash - Older standard, similar to 1633A. Well characterized for about 40 elements (14).

5. NBS SRM 1571 Orchard Leaves - Certified by NBS for 25 elements, with information values for 12 others. Values quoted for other elements by many other investigations.
6. NBS SRM 1577 Bovine Liver - Certified by NBS for 16 elements, with information values for 13 others. Values quoted for other elements by several investigators.
7. SRM 1645 River Sediment - An SRM presently under development.
8. SRM Oyster - A new oyster standard now under development.
9. Freeze-dried Saliva - Not a standard. Collected and freeze-dried by Dr. Robert Henkin, Georgetown University Medical Center.

In addition, to the above, we have irradiated samples of particles, ores and slimes from a copper smelter, atmospheric particles and lichens, but have not begun to analyze their spectra yet. A listing of the elements so far observed in some of the standards is given in Table 4.

Table 4. Elements with Identified Lines in Prompt γ -Ray Spectra^a

Element	<u>Fly Ash</u> 1633A and 1633	<u>Coals</u> 1632, 1632A and 1635	<u>Orchard Leaves</u> 1571	<u>River Sediment</u>	<u>Oyster</u>	<u>Saliva</u>
H	D	D	D	D	D	D
B	D	D	D	D	D	D
C	Bk	D	D	-	D	D
N	Bk	Bk	-	-	D	D
Na	D	-	-	D	D	D
Mg	D	D	-	-	-	D
Al	D	D	D	D	D	D
Si	D	D	-	D	-	-
P	D	-	-	-	-	D
S	D?	D	D	D	D	D
Cl	D	D	D	-	D	D
K	D	D	D	D	D	D
Ca	D	D	D	D	-	-
Ti	D	D	-	D	-	-
V	D	-	-	D	-	-
Cr	-	-	-	D	-	D
Mn	D	-	-	-	-	-
Fe	D	D	-	D	Bk	-
Zn	-	-	-	D	-	D?
Br	-	-	-	-	-	-
Cd	D	D	D	D	D	D
I	Bk	Bk	-	-	D	-
In	-	-	-	-	-	-
Sm	D	D	-	D	D	D
Gd	D	D	-	D	-	-
Dy	D?	-	-	-	-	-
Pb	-	-	-	-	D?	-

^aAll lists incomplete, as spectra are not completely analyzed.

D = Definitely observed above background.

Bk = Observed at about background level.

D. Energy Calibration Lines

With the prompt spectrum from 0 to 11 MeV spread out over 16,384 channels and our ability to locate centroids of reasonably large peaks to ± 0.5 channel or better, we should be able to determine peak energies to an accuracy of about ± 0.4 keV. This is important when dealing with such complex spectra, as highly accurate energies can eliminate ambiguities as to identities of lines. There are many accurately known lines from radioactive decay up to about 3.5 MeV, but above that point, we were surprised to find very few capture lines known to a stated energy of ± 1 keV or better as listed in compilations, especially Ref. 13. One of the potentially most useful calibration spectra would be that of prompt γ rays from capture in nitrogen, as it contains strong lines spanning the range from 1885 to 10,830 keV and nitrogen is observable in many samples. Its spectrum has been carefully investigated by many workers and the energies of its lines are quoted to high accuracy. The problem is that the various sets of data disagree outside of their quoted errors, as illustrated in Table 5. As illustrated there, disagreements among previous works (Cols. 2, 3 and 4) are often 2 to 3 keV.

We have redetermined the energies of the nitrogen lines by careful calibration of the system at low energies followed by use of the "bootstrap" technique (15). The latter method takes advantage of the fact that the energy difference between a full energy peak and its double-escape peak is quite accurately known (equal to twice the rest mass of the electron, 1022.012 keV, Ref. 13). Thus, for example, one

Table 5. Energies of Major Lines from Neutron Capture by Nitrogen (keV)

Line No.	Rasmussen et al. (11) (all ± 1 keV)	Greenwood et al. (Ref. 15)	Carter et al. (Ref. 16)	This work
1	10,827.7	-	10,829.4 $\pm$ 0.5	10,829.8 $\pm$ 0.2
2	7,299.5	-	7,298.2 $\pm$ 0.6	7,299.4 $\pm$ 0.4
3	6,321.4	6,322.0 $\pm$ 0.4	-	6,322.5 $\pm$ 0.2
4	5,560.3	5,562.6 $\pm$ 0.4	5,561.5 $\pm$ 0.5	5,562.2 $\pm$ 0.3
5	5,532.0	5,533.5 $\pm$ 0.5	5,532.7 $\pm$ 0.4	5,533.5 $\pm$ 0.3
6	5,296.7	5,298.3 $\pm$ 0.3	5,296.7 $\pm$ 0.4	5,298.4 $\pm$ 0.3
7	5,267.1	5,269.6 $\pm$ 0.3	5,267.8 $\pm$ 0.3	5,269.5 $\pm$ 0.2
8	4,507.6	4,509.2 $\pm$ 0.3	-	4,509.3 $\pm$ 0.2
9	3,675.4	3,678.1 $\pm$ 0.2	-	3,678.1 $\pm$ 0.2
10	3,530.5	3,532.3 $\pm$ 0.2	3,532.7 $\pm$ 0.5	3,532.2 $\pm$ 0.2
11	2,519.0	2,518.0 $\pm$ 0.2	-	2,520.6 $\pm$ 0.2
12	1,887.9	1,884.9 $\pm$ 0.2	-	1,884.8 $\pm$ 0.2

can determine the energy of the 2521 keV line quite accurately from the position of its double-escape peak at 1498 keV, where the energy scale is accurately calibrated from radioactive decay lines and the H capture line at 2223.29 ± 0.07 keV (13). Once the 2521- and 1855-keV lines are accurately known, they can be used to calibrate the region of the double-escape peaks from the 3532- and 3678-keV lines that fall at 2510 and 2656 keV, respectively. One can work all the way up to the 7299-keV line using the bootstrap method. The results of our use of this approach are given in the last column of Table 5. Except for the γ ray at 2521 keV, there is excellent agreement between our results and those of Greenwood et al. Rasmussen's energies are off by 2 to 3 keV over much of the range of energies.

The 10,830-keV line cannot be reached by bootstrapping, but can be determined in another way. The decay scheme of γ rays emitted following the neutron capture is known (13). The 10,830-keV γ ray is emitted from the capture level to the ground state. Also, various combinations of the lower energy lines in Table 5 are emitted between the capture level and the ground state. The sums of the energies of these γ -ray cascades, plus recoil energies of the nucleus (4.2 keV for 10.8 MeV line) should all equal the level energy, if the γ -ray energies are accurate. We show the calculated level energies from the cascades in Table 6. Our own data give a consistent level energy varying only between 10,833.9 and 10,834.1 keV, in good agreement with the Q value for neutron capture determined from very accurate (d,p)-reaction measurements, $10,834.8 \pm 0.8$ keV (13). Therefore, we adopt our value of the level energy, $10,834.0 \pm 0.2$ keV, corresponding to an energy of $10,829.8 \pm 0.2$ for the highest energy nitrogen line.

Note in Table 6 that Greenwood's level energies vary by only 1.1 keV, whereas those of Rasmussen and Carter vary by 2.8 and 2.1

Table 6. Level Energies Calculated from γ -Ray Cascades (keV)

Cascade (numbered lines from Table 5)	Rasmussen (Ref. 11)	Greenwood (Ref. 15)	Carter (Ref. 16)	This work
1	10,831.9 $\pm$ 1	-	10,833.6 $\pm$ 0.5	-
4+ 7	10,829.6 $\pm$ 1.4	10,834.4 $\pm$ 0.5	10,831.5 $\pm$ 0.6	10,833.9 $\pm$ 0.3
5+ 6	10,830.8 $\pm$ 1.4	10,833.9 $\pm$ 0.5	10,831.5 $\pm$ 0.6	10,834.0 $\pm$ 0.4
2+10	10,832.4 $\pm$ 1.4	-	10,833.3 $\pm$ 0.8	10,834.0 $\pm$ 0.5
3+ 8	10,831.1 $\pm$ 1.4	10,833.3 $\pm$ 0.5	-	10,833.9 $\pm$ 0.3
7+9+12	10,832.1 $\pm$ 1.7	10,834.3 $\pm$ 0.5	-	10,834.1 $\pm$ 0.35
Adopted level energy				10,834.0 $\pm$ 0.2
Corresponding $E_{\gamma 1}$				10,829.8 $\pm$ 0.2

Table 7. Energies Measured for Silicon Capture γ Rays (keV)

Rasmussen et al. (Ref. 11)	Kennett (given in Ref. 13)	This work
7,199.3 $\pm$ 1.0	7,202.1 $\pm$ 1.0	7,199.8 $\pm$ 0.3
6,380.1 $\pm$ 1.0	6,383.1 $\pm$ 1.0	6,380.2 $\pm$ 0.3
4,934.3 $\pm$ 1.0	4,935.8 $\pm$ 1.0	4,934.0 $\pm$ 0.2
3,954.9 $\pm$ 1.0	3,956.0 $\pm$ 1.0	3,957.8 $\pm$ 0.2

keV, showing that they are not internally self-consistent.

We have also calibrated the Si capture γ rays using the bootstrap method, obtaining the results listed in Table 7. Again, we see that the previous sets of data disagree strongly with each other and with our values. Silicon will also provide a valuable set of calibration lines, as Si is quite abundant in most crustal samples and its lines are quite strong in the spectra (see Fig. 5).

Before publishing our results in final form, all γ -ray energies will be determined accurately using these calibration lines. However, we just recently determined their values, so we've not had time to adjust all observed lines to the latest energy scale. Therefore, there may be inconsistencies among the energies quoted in this report, but they will be corrected later. Energies given in Fig. 5 are accurate.

E. Quantitative Analyses

1. Overview

The eventual aim of this project is, of course, that of determining concentrations of as many elements as possible in a wide range of materials. In addition to identifying γ -ray lines in the spectra from various samples, we have also begun to make tests of the quantitative application of the method. All samples run in the system have known weights, typically of about 1 g and are formed into pellets of 1.3-cm diam, which are sealed in Teflon film and placed entirely within the central, uniform portion of the neutron beam. The count rates under peaks associated with specific elements are compared with count rates under the same peaks in spectra taken with known masses of elemental standards in the beam. Before and after each run, we take a short count of a particular Cr standard. The count rate under its peaks is a measure of both the flux and the

detector geometry. By keeping track of the Cr counting rate associated with each standard, we can use that standard for the analysis of samples taken under different conditions of flux and geometry. This is important, as the reactor does run at different power levels, which changes the flux. Also, when we realign the detector system, it doesn't always have the same geometry.

In the following sections, we discuss tests of various aspects of the quantitative measurements: the use of Cr standards to monitor flux and geometry, reproducibility in the placement of samples in the beam, and self-absorption of neutrons by standards of high cross section. Finally, we report values for a few elements that we have measured in several materials and compare them with previous values. Since we have not yet identified all of the lines in the spectra and run standards of all elements that may be observable, the reported concentration values are somewhat tentative, as some peaks used in the determinations may contain undiscovered interferences. However, in most instances, we've obtained the same concentration values from several different lines, so in those cases, the values are probably correct.

2. Use of Chromium Flux and Geometry Monitor

Since the reactor changes its power level and also must be shut down occasionally and our apparatus completely removed from the reactor top, a Cr standard is being used to monitor changes in our relative detection efficiency. The standard weighs 0.05g and has to be irradiated for about 15 min to obtain good statistics. The use of the monitor is illustrated in Table 8, where we show the ratio of count rates under several peaks to the rates measured before any disturbance of the system. Column 2 shows the ratios observed after a power reduction

Table 8. Ratios of Areas under Several Peaks of Cr Standard Following Changes of Power Level and/or System Realignment

E _γ (keV)	Ratio of Count Rate to Initial 9.9-MW Run	
	Change to 9.0 MW	After shutdown, realignment and power raised to 9.9 MW
749	0.91±0.01	1.29±0.01
834	0.91±0.01	1.32±0.01
1784	0.94±0.03	1.31±0.04
1899	-	1.25±0.07
2238	0.93±0.03	1.34±0.04
5617	0.95±0.10	-
8372	0.98±0.04	1.34±0.04
8884	0.97±0.04	1.29±0.04

from 9.9 to 9.0 MW and Col. 3 shows the ratios after a shutdown, realignment of our system and return to 9.9-MW operation. As can be seen the ratios are in reasonable agreement over the whole energy range, especially for Col. 3. The ratios of about 1.3 in Col. 3 result from our achieving higher efficiency by more careful alignment of the sample holder and collimator system after the shutdown. The good results for these comparisons mean that we can use the Cr standard for intercomparison of spectra taken under different conditions. Most important, it means that we do not have to run all of the elemental standards after each change of the system. We now routinely run the Cr standard frequently between the taking of other spectra.

3. Reproducibility of Sample Placement

We investigated errors arising from placement of the samples in the beam by repeated irradiations of a Co standard. The count rates under eight of the prominent peaks are listed in Table 9 for five irradiations. As indicated there, the standard deviation of sample placement is about 3.4%. We believe this error can be reduced somewhat by improvements on the sample holder and the use of more care in placing samples.

4. Self-Absorption of Flux

Since we are able to use much larger samples in PGAA than in INAA, a potential problem for quantitative work is the self-absorption of neutrons by the sample or standards, particularly the latter for elements with very large cross sections. We can estimate the size of the effect by a calculation that assumes a flux ϕ perpendicular to a target of surface density, d (in mg/cm^2), by calculating the average flux throughout the material, $\bar{\phi}$, and the flux reduction factor, R , equal to $\bar{\phi}/\phi$. The expression for R is:

$$R = \frac{1}{\beta d} [1 - e^{-\beta d}],$$

where $\beta = N_0 \sigma / M$, with N_0 = Avogadro's number, σ = neutron-capture cross section, and M = atomic mass number of the element. We've used this expression to calculate R values for various thicknesses of several elements and the thickness of standards that should cause a reduction of the average flux by 1, 5 and 10% (corresponding to βd of 0.021, 0.10 and 0.21, respectively). The latter values for several elements are shown in Table 10.

In Table 10, we see that one can use very thick samples of elements such as Fe, which have modest cross sections, before

Table 9.

Reproducibility of Placing a Sample in the Beam^a Using the Eight Most Intense Prompt γ -Rays of Co

E_{γ} (keV)	1 (c/s) ^b	2 (c/s) ^b	3 (c/s) ^b	4 (c/s) ^b	5 (c/s) ^c	$\bar{X}$	σ	% Error
230	54.0	54.0	53.5	54.4	49.6	53.1	2.0	3.8
277	45.6	45.8	44.8	44.0	42.5	44.5	1.3	3.0
447	16.9	16.8	16.7	17.2	15.5	16.6	0.63	3.8
497	10.5	10.9	10.7	10.7	9.87	10.5	0.39	3.7
555	26.3	26.1	25.9	27.1	24.2	25.9	1.1	4.1
785	7.84	7.89	7.65	8.06	7.30	7.75	0.29	3.7
183	3.16	3.18	3.11	3.22	3.00	3.13	0.085	2.7
1515	3.85	3.78	3.89	3.77	3.68	3.79	0.081	2.1
Average % Error								3.4

^aThe samples was completely removed from the beam, the sample box and the sample holder between each run.

^bThese were irradiated for 1/2 hour back to back over a 2 1/2 hour period.

^cThis was irradiated for 2 hours about 5 days before the other four spectra were taken.

Table 10. Surface Densities of Various Elements that Reduce Flux by 1, 5 and 10%^a

Element	σ (barns)	β (cm ² /g)	Surface density (mg/cm ²) to give % reduc.		
			1%	5%	10%
B	752	42	0.5	2.5	5
(as H ₃ BO ₃)			2.9	14	29
Fe	2.6	0.028	750	3600	7500
Cd	3620	19.4	1.1	5.2	11
Sm	5840	23.3	0.9	4.3	9
Gd	39100	149	0.14	0.7	1.4

^aCalculated for targets perpendicular to beam. If placed at an angle θ , surface densities should be divided by $\cos\theta$.

self-absorption becomes appreciable. On the other hand, as little as 1.4 mg/cm^2 of Gd would cause a 10% reduction of the average flux.

We have tested the calculations by placing standards of various thickness in the beam and checking the count rate of one or more prominent peaks. For example, Fig. 7 shows the count rate of two Fe lines vs. mass over an area of about 1 cm^2 . As predicted, there is no apparent fall-off of points from the line. By contrast, Fig. 8 shows a similar plot for boron as H_3BO_3 deposited on an area of 1.33 cm^2 . As indicated by the predicted points, the fall-off of count rate with increasing thickness is approximately in agreement with the calculations. Standards for materials with very large cross sections are made by pipetting a dilute solution as uniformly as possible over a Whatman 541 filter, which is then formed into a pellet of 1.33 cm^2 area. The slight disagreement between the predicted and observed flux reduction in Fig. 8 probably comes from non-uniformities of placement of the solution on the filter. Similar curves taken for Gd, Sm and Cd standards confirm the calculations of Table .

We've also been concerned about self-absorption in samples. To check on this, we summed the β values for many elements in NBS Fly Ash (weighting each element by its concentration). According to this calculation, the effective β for fly ash is $0.027 \text{ cm}^2/\text{g}$, about the same as for pure Fe, so we don't expect self-absorption to be any more serious than indicated for Fe in Table 10. In the case of fly ash and several of the samples under study, we've obtained the same concentration values from samples of several different sizes up to several grams, indicating that self-absorption is not a problem for them.

Figure 7. Activity versus Sample Weight of Iron

Fig. 8. Calculated and observed count rate versus thickness for 478-keV line from H_3BO_3 samples.

5. Results of Analyses

Quantitative analyses for up to about 15 elements in several materials have been performed using the techniques described in the preceding sections. In each case the analysis has been done relative to one or more standards for the element. Whenever possible, several different lines of the element have been used. When one or more lines gave results in disagreement with the others, this was carefully checked. In a number of cases, the peak used had not been accurately fitted by the computer program and more consistent results were obtained by hand-fitting of the peaks. (This should be improved with the program now under development.) Contributions of background and known interferences were removed from the peaks used; however, we cannot be certain that all interferences have been removed until all peaks in the spectra have been identified and spectra of their standards taken, but the generally good agreement between different lines for each element and the agreement of final results with other reported concentrations suggest that most interferences have been removed. Table 11 lists the γ rays used for analyses and the major interferences removed.

Our presently measured concentrations of various elements in several SRMs are listed in Table 12 to 16, where they are compared with NBS Certified Values or other reported values if available. One should not take our finals as being completely final, as there are still some outstanding questions about interferences in certain lines, the correct weights of standards (for some that are hygroscopic), and possible contaminants in the standards. Nevertheless, the overall agreement between our values and the previous data is generally quite gratifying.

On NBS Fly Ash (Table 12), we have good agreement on most values. There is still some question about the correct B value. The Cd agreement with NBS is quite good.

In the case of SRM 1632 Coal (Table 13), again K is somewhat high, but other elements agree well.

Data for the new Eastern Coal (1632A) are given in Table 14. The agreement throughout is quite good except possibly for Sm and Si. Since Si values from PGAA are quite good for other standards, we feel it is probably correct here. The other value was determined by 14-MeV neutron activation. The Western coal is much more difficult to analyze as it is hygroscopic and it has much lower concentrations of many elements. The agreement is reasonably good for most elements except Cd. It would appear that, at these very low Cd levels there is an interference that we haven't removed.

In Table 16, we can't assess the quality of the data, as there are no other data for comparison. The K value for river sediment may be too high, as we had a problem with a hygroscopic standard that is now being checked.

Table 11. Gamma Rays Used for Analyses for the Elements

Element	E _γ (keV)	Major Interferences, Comments
H	2223 1712 (SE)	
B	478	Doppler-broadened, integ. by hand; must remove Na 472, and, sometimes, Cl 477
C	4945 1261	Fe, Sm, Gd (in crustal spls.)
N	10830+10320 (SE) 7299 6322 5533 5269	Clean, but poor statistics
Na	2574D } 1369D } 874 }	Must make careful time corrections for growth of 15-hr species Sm (in crustal samples) (+472 in high Na samples)
Al	7723 6702 1779D	Usually at equilibrium unless v. short run
Si	3910 3540+2092+1273 3028	
P	1071 636	
S	5420 3219 2930 2379 } 840 }	Best lines
Cl	7792 7414 6905 (SE) 6111 5089 (DE) 1957 1949 1164 516 785+788	Contains Cl escape peaks Doublet integrated together

Table 11. Gamma Rays Used for Analyses for the Elements (Cont'd.)

Element	E_{γ} (keV)	Major Interferences, Comments
K	770	About 5% Gd in crustal samples
Ca	1942	
Ti	1381 341	
V	646, 1434D	
Fe	8787 7646 7632 7135SE 7121SE 352	
Cd	558 651	Sm, Gd, Fe, possibly others
Sm	736 505 439 333	
Gd	1107 976 964 947 182	

Table 12. Analysis of NBS Fly Ash (SRM 1633)

Element (conc. unit)	Concentration			
	This work (1 spl.)	Ondov et al. (Ref. 14)	NBS	Other Values
H (%)	0.35±0.03	-	-	-
B (ppm)	443±5	-	-	493±10 (7) 434±9 ^a
Al (%)	13.0±0.2	12.7±0.5	-	12.3±0.6 (17)
Si (%)	24.5±1.1	21±2	-	20±1.6 (17)
S (ppm)	4000±400	-	-	4400±100 (7)
K (%)		1.61±0.15	-	1.65±0.05 (17)
Ca (%)	4.9±0.2	4.7±0.6	-	4.5±0.4 (17)
Ti (ppm)	7210±95	7400±300	-	7300±300 (17)
Fe (%)	6.22±0.08	6.2±0.3	-	6.2±0.1 (17)
Cd (ppm)	1.40±0.16	-	1.4±0.06	1.6±0.2 (7)
Sm (ppm)	13.0±0.3	12.4±0.9	-	12.1±1.0 (17)
Gd (ppm)	11.7±0.4	-	-	-

^aS. Carpenter, NBS, private communication (charged-particle track method)

Table 13. Analysis of NBS Coal (SRM 1632)

Element (conc. unit)	Concentration			
	This work (2 spls.)	Ondov et al. (Ref. 14)	NBS	Other Values
H (%)	4.4±0.2	-	-	-
B (ppm)	46.1±0.3	-	-	47.5±0.5 (7); 43 (18)
C (%)	59.4±0.6	-	-	-
Al (%)	1.8±0.2	1.85±0.13	-	1.72±0.09 (19)
Si (%)	3.1±0.3	-	3.2 ^a	-
S (%)	1.42±0.5	-	-	1.32±0.07 (7)
Cl (ppm)	900±25	890±125	-	860±54 (18)
K (%)	0.33±0.02	0.28±0.03	-	0.28±0.03 (18)
Ca (%)	0.42±0.06	0.43±0.05	-	0.70 (18)
Ti (ppm)	860±80	1100±100	800 ^a	1100 (18)
Fe (%)	0.89±0.04	0.84±0.04	0.87±0.03	0.93±0.08 (18)
Cd (ppm)	0.22±0.05	-	0.19±0.03	0.2±0.05 (7) 0.21±0.01 (18)
Sm (ppm)	1.60±0.06	1.7±0.2	-	1.6±0.2 (18)
Gd (ppm)	1.47±0.12	-	-	-

^aNot certified; information value.

Table 14. Analysis of NBS Coal (SRM 1632A, Bituminous, Eastern)

Element (conc. unit)	Concentration		
	This work (2 spls.)	This laboratory (other methods)	NBS
H (%)	3.89±0.12	-	-
B (ppm)	50.9±0.5	-	-
C (%)	65±4	-	-
Al (%)	2.90±0.05	2.95±0.28	3.07 ^a
Si (%)	6.05±0.20	3.2±0.5	-
S (%)	1.59±0.04	-	1.64 ^a
Cl (ppm)	766±30	790±30	-
K (%)	0.47±0.01	0.42±0.02	-
Ca (%)	0.24±0.02	0.24±0.02	-
Ti (ppm)	1480±30	1610±60	1750 ^a
Fe (%)	1.17±0.04	1.16±0.03	1.11±0.2
Cd (ppm)	0.15±0.03	-	0.17±0.02
Sm (ppm)	2.10±0.05	2.95±0.10	-
Gd (ppm)	1.9±0.2	-	-

^aNot certified; information value.

Table 15. Analysis of NBS Coal (SRM 1635, Subbituminous, Western)

Element (conc. unit)	Concentration		
	This work (2 spls.)	This laboratory (other methods)	NBS
H (%)	5.0±0.3	-	-
B (ppm)	86±3.0	-	-
C (%)	61.5±3.0	-	-
Al (%)	0.47±0.02	0.31±0.03	0.32 ^a
Si (%)	0.55±0.03	0.56±0.07	-
S (%)	0.29±0.03	-	0.33 ^a
Cl (ppm)	26±3	26±4	-
K (ppm)	100±20	123±15	-
Ca (%)	0.43±0.03	0.55±0.05	-
Ti (ppm)	140±20	206±11	200 ^a
Fe (%)	0.19±0.05	0.23±0.02	0.239±0.005
Cd (ppm)	0.15±0.03	-	0.03±0.01
Sm (ppm)	0.22±0.03	0.30±0.04	-
Gd (ppm)	0.20±0.05	-	-

^aNot certified; information values

Table 16. Analysis of NBS Fly Ash (SRM 1633A) and River Sediment (1645)

Element (conc. unit)	Concentration - This work (1 spls. each)	
	Fly Ash	River Sediment
B (ppm)	36.2±2.0	30.4±0.6
Na (ppm)	6100±400	-
Al (%)	13.6±0.5	2.3±0.1
Si (%)	23±1.5	50±1
P (%)	1.6±0.4	-
S (%)	0.29±0.04	0.40±0.03
Cl (ppm)	27±10	-
K (%)	2.00±0.15	1.37±0.03
Ca (%)	1.23±0.15	3.0±0.1
Ti (%)	0.81±0.04	0.059±0.05
V (ppm)	230±20	-
Cr (%)	-	3.13±0.05
Mn (ppm)	290±30	-
Fe (%)	9.0±0.5	10.1±0.6
Cd (ppm)	1.02±0.14	7.6±0.2
Sm (ppm)	15.3±1.1	1.29±0.05
Gd (ppm)	14.1±0.5	0.91±0.06

IV. SUMMARY AND CONCLUSIONS

Although there is still a considerable amount of development work to be done on PGAA, it is already clear that the method is going to be very useful in many applications. From our work to date it appears that about 20 elements will be measurable in most complex samples. (This is not entirely the same set of 20 elements in all samples.) Some additional elements may be observable after we finish identification of all usable lines. Furthermore, the quantitative tests we have done on samples of known composition indicate that the method will be quite reliable if the peaks for an element are large enough to give good statistics and one has identified all significant interferences.

It is appropriate to compare our results with those from previous studies. In their 1968 study, Lombard and Isenhour (4) determined detection limits for 18 elements measured individually in pure water solutions. While this gave some indication of the value of the method, one can't learn too much from detection limits of pure elements. Of the 18 elements in their list, we have observed only seven thus far among our samples (Gd, I, Sm, B, Cd, Cl, Cd, possibly Dy). Their 18 elements were those calculated to have the lowest detection limits. These calculations and single-element experiments, however, don't predict which elements one will see because (1) they don't take into account the composition of real samples and (2) they usually predict the greatest sensitivity for low energy γ rays because of typically greater intensities (photons/100 captures) and detector efficiencies. Regarding (1), when we made predictions of observable elements, we

weighted the raw sensitivities by the crustal abundance pattern of the earth. Thus, among our first 18 predicted elements, we have observed all but three (Eu, Sc, Nd) in fly ash samples. Of course, in more "organic" samples (coal, orchard leaves, oyster, etc.), we see a somewhat different group of elements (including C, H, N).

Regarding point (2), the predictions of greatest sensitivity at low energy fail to take into account the fact that many other elements in a complex sample also have their greatest intensities at low energy. Furthermore, that region also has the most general background from Compton events, backscatter, and bremsstrahlung (see Fig. 5, parts 1-3). By contrast, although absolute counting rates are generally lower at high energies, the backgrounds and densities of lines are much lower, so it's often easier to detect an element via high energy lines (see Fig. 5, parts 4 and 5). Therefore, to achieve optimum detection of all elements, one needs a detection system that is effective over the whole range of energies up to 11 MeV. It should be noted that we may be able to lower the detection limits for species emitting low energy lines by cleaning up that portion of the spectrum. The use of Compton suppression, for example, may make additional low energy lines observable.

Henkelmann and Born (6) performed work similar to that of Lombard and Isenhour, measuring limits of detection for 26 elements; however, they considered both high and low energy lines, in every case indicating lower detection limits at low energy. Of those 26 elements, however, we have observed only 9, and we observe several not considered by them (H, C, N, Na, Al, Si, S, P, K, Ca and I). They show a spectrum of monazite sand, in which they claim to see all of the naturally occurring rare earths except Ce, but the peaks are not labelled in the

spectrum. Note that monazite sand is a very unusual sample, containing more than per cent levels of some rare earths. This paper does not give one an indication of what one might be able to see in more normal types of samples.

Comar et al. (5) took prompt γ -ray spectra of a wide range of biological samples, but they extracted lines of very few elements from their spectra: B, Na, Cl and K in blood; N, P, Cl and Ca in bone; and H, B and Cl from plants. It is not clear why they didn't push the technique beyond that point.

More recently, Journey et al. (7) at Los Alamos studied the application of PGAA using a system of efficiency comparable with ours, except that samples are placed in the thermal column. Their samples are subjected to a much greater flux than ours, but this is roughly compensated by much lower geometry of the detector outside of the reactor. In one paper, the Los Alamos group demonstrated their ability to measure B and Cd reliably in a wide range of samples and, in the second paper, S in many samples. They are aware of Na interference (at 472 keV) in the Doppler-broadened B 478-keV peak, but make no mention of Cl interference. The Cl peak is significant in our oyster spectrum, but is probably much less so in their samples, as they achieve excellent agreement with previous measurements of B concentrations. Likewise, they do not indicate any interference problems for the Cd 558-keV line, but our present data suggest that there may be significant interferences. In part, that may be an artifact caused by Cd contamination in our standards. However, we believe there is a contamination problem that becomes significant at very low Cd concentrations, as our first value for Western coal (SRM 1635) is much higher than the certified value of 30 ± 10 ppb. Our other measured values for Cd, which were higher and not corrected for interferences, agree well

with other values for the same samples. The values reported by Gladney et al., were also high (minimum 200 ppb) and in reasonable agreement with NBS values. We will clarify the question of interferences in the Cd peak by further study of elemental standards. The Los Alamos group show peaks of Na, Sm, Cl, Ca and K in their spectra, but do not report analyses for them.

By continuing our investigation of the complete energy spectra of various samples and several standards for each element, we feel it will be possible to develop reliable procedures for the analyses of many types of samples for the order of 25 elements, several of which are difficult or impossible to measure reliably by other methods and yet important for various reasons, e.g., Cd and B. The PGAA method is useful for an interesting mix of elements: some present in very minute amounts, such as Sm, Gd and Cd, but other major elements such as C, H, N, Si, Al and Fe. The collection of major elements is approximately the same group as measured in classical geochemical studies, but without the necessity to dissolve the samples. The Cd measurements are very important, as Cd is toxic at low concentrations, but most methods for measuring its concentrations at low levels are unreliable (14). The importance of measuring B concentrations may be enormous, for example, in studying low levels of the element in semiconductor materials and to study its presence in soils (which are often deficient), to name just two examples. Sulfur measurements in bulk samples are also important, especially in studies of air pollution and the source materials of it. The major competitive method is γ -ray analysis for light elements (GRALE) of Edward Macias of Washington University. The application of that method to bulk samples is limited by the range of charged particles used to excite γ rays by inelastic scattering.

One should not consider PGAA as a technique that must stand by itself. Obviously, if one has the reactor and counting equipment needed for PGAA, he can also perform INAA measurements which, together with PGAA, would yield concentrations of about 40 elements by completely instrumental methods. Several important elements are measurable by PGAA that are difficult or impossible to measure by INAA: H, B, C, N, Si, P, S, Cd and Gd. We've also found the rapid turnaround time of PGAA to be very convenient: we obtain results from experiments the same day rather than having to wait two or three weeks as in the "longs" part of INAA.

V. THESES, ADDRESSES AND PUBLICATIONS

A. Theses

1. Paul Solomon, "Neutron-Capture γ -Ray Analysis: A New Analytical Technique", B.S. Honors Thesis, Department of Chemistry, University of Maryland. (Also submitted in competition for the ACS Division of Nuclear Chemistry and Technology Coryell Award for Outstanding Undergraduate Research in Nuclear Chemistry.)

B. Talks

1. G. E. Gordon, D. L. Anderson, M. P. Failey, W. B. Walters, W. H. Zoller and R. M. Lindstrom, "Prompt Gamma-Ray Activation Analysis", Invited Paper, 3rd Int. Conf. on Nucl. Methods in Environmental and Energy Research, Univ. of Missouri, Columbia, Mo., Oct. 1977.
2. D. L. Anderson, M. P. Failey and W. H. Zoller, "Rapid Analysis of Short-Lived Neutron-Irradiation Products Using a Mini-computer-Based Pulse-Height Analyzer", Amer. Nucl. Soc. Topical Meeting, Mayaguez, Puerto Rico, Apr., 1978.
3. Expect talk on new results at Third Int. Symposium on Neutron Capture Gamma-Ray Spectroscopy and Related Topics, Brookhaven National Laboratory, Sept. 18-22, 1978.

C. Publications

1. G. E. Gordon, D. C. Anderson, M. P. Failey, W. B. Walters, W. H. Zoller and R. M. Lindstrom, "Prompt Gamma-Ray Activation Analysis", Invited Paper, 3rd Int. Conf. on Nucl. Methods in Environmental and Energy Research, Univ. of Missouri, Columbia, Mo., Oct. 1977. (in press).

Two papers in preparation: One describing general characteristics of method and a second in which results for new NBS standard coals (SRM 1632A and 1635) obtained by PGAA, INAA, IPAA and limited work with 14-MeV neutrons are given.

VI. PERSONNEL

1. Principal Investigators

Prof. Glen E. Gordon, Department of Chemistry, University of Maryland

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Prof. William B. Walters, Department of Chemistry, University of Maryland

Dr. Richard M. Lindstrom, cooperating scientist from Center for Analytical Chemistry, National Bureau of Standards (at no cost to contract).

2. Other Participants

Dr. David Anderson, Research Associate, Department of Chemistry, University of Maryland

Mr. Michael P. Failey, Graduate Student, Department of Chemistry, University of Maryland

Mr. Paul Solomon, Undergraduate Student, Department of Chemistry, University of Maryland (terminated upon graduation, now a graduate student at University of Arizona, Tucson).

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