REPOSITORY Oak Ridge Operations Records Holding Area
COLLECTION Documents 1944-94
712365
941 (R)

U.S. DEPARTMENT OF ENERGY

memorandum

DATE OCT 12 1979

REPLY TO ATTN OF ER-162

SUBJECT Justification for Acceptance of Renewal Proposal from the University of Maryland (Gordon, Zoller & Walters) for Contract No. DE-AS05-76ER05173

TO: James S. Kane, ER-10

BOX No. B-92-5 Bldg. 2714-H
FOLDER Contract No. DE-AS05-76ER05173 Univ. of MD

Title:

"Non-Destructive Determination of Trace-Element Concentrations"

Scope:

The application of neutron-capture prompt gamma-ray analysis for the determination of trace elements which are not determinable by neutron activation.

Recent Progress:

They continued the development and testing of the neutron-capture prompt γ-ray activation analysis (PGAA) method. A wide range of NBS Standard Reference Materials, USGS Standard Rocks and other materials have been analyzed in order to identify elements whose lines can be observed, determine interferences and detection limits for each important γ ray of observable elements and measure concentrations of observable elements for comparison with certified or other previous results.

The results of these tests have been quite favorable. In most types of "crustal" samples (rocks, minerals, coal, fly ash, etc.), concentrations of 16 to 20 elements can be determined. Although PGAA is very sensitive for several trace elements (e.g., B, Cd, Nd, Sm and Gd), it is much more of a major element method than off-line instrumental neutron activation analysis (INAA). One can, for example, measure concentrations of most of the major elements usually measured by geochemists in rocks and minerals. This is demonstrated by the fact that when one sums the masses of the common oxides of the measured elements, the sum is typically from 95 to 99% for most rocks and fly ashes. If the samples contain much organic material (e.g., coals, biological samples), H, C, N and S can usually be measured. Because of their lower concentrations, many elements that are observable in crustal materials cannot be measured in biological samples.

Another important result of this work has been finding that the accuracy of PGAA is considerably better than that of INAA for many elements that are measurable by both methods. There are several reasons for this including the avoidance of timing errors, the ability to use several prompt lines for most elements and the ability to collect data for very long periods to build statistics. The high accuracy also indicates that their methods for positioning samples, using a Cr standard to normalize flux and geometry variations and avoiding self-absorption problems have been successful.

Cig

1079127

During the year they achieved operation of the full detection system on-line by connecting up the NaI(Tℓ) annulus detector to operate in the Compton-suppression and pair modes. Both types of spectra are much simpler than the singles spectra at high energies. This makes it possible to remove ambiguities in the identities of lines and detect interferences between single- and double-escape peaks with full energy peaks of lower energy γ rays. At lower energies, although the Compton-suppressed spectra do not look dramatically different from the singles spectra, the general backgrounds due to Compton events are reduced enough to lower the detection limits for various elements by an average factor of 1.7 in coal samples.

They have investigated the possible use of PGAA as the detection system for stable isotope tracing in medical studies of people who cannot be injected with radioactive tracers; pregnant women and persons under age 18. Present estimates are that experiments would require such large quantities of stable isotope tracer as to be nearly prohibitively expensive. However, further improvements may be possible, e.g., the use of PGAA and INAA.

The utility of PGAA in the study of volcanic materials and of floc from a water treatment plant has been demonstrated.

Publications:

1. D. L. Anderson, M. P. Failey, W. H. Zoller and G. E. Gordon, Neutron-Capture Prompt Gamma-Ray Activation Analysis: Multi-Element Measurements on Various Materials, in Neutron-Capture Gamma-Ray Spectroscopy, R. E. Chrien and W. R. Kane, eds. (Plenum Press, New York, 1979), pp. 546-548.

2. M. P. Failey, D. L. Anderson, W. H. Zoller, G. E. Gordon and R. M. Lindstrom, Neutron Capture Prompt γ-Ray Activation Analysis for Multi-Element Determination in Complex Samples, Anal. Chem. (in press, 1979).

Two additional papers are in preparation.

Proposed Research:

During the coming year, they propose to focus their efforts on reducing backgrounds and increasing sensitivities for observation of various γ rays, especially at low energies. With these improvements they hope to be able to lower detection limits for elements now observable and to extend the PGAA method to additional elements. They also plan to extend the analytical studies to new classes of samples, with emphasis on samples relevant to energy sources. In addition, they plan to up-grade their data handling capabilities.

The limits of detectability for elements with major γ-ray transitions below 400 keV are large because of the presence of a large quantity of γ radiation scattered from the beam by the target itself. As this radiation originates at the target, the Compton suppression system does not reduce it significantly. Over 99.9% of this γ radiation can be eliminated by placing an oriented single crystal of very highly purified Bi cooled to liquid nitrogen temperature in the beam. Moreover, 94% of the fast neutrons can also be eliminated while the flux of thermal neutrons would be reduced by only 50%. The reduction of the low energy background would lower the limits of detectability for a number of important elements.

Although the loss of 50% of the neutrons will reduce the efficiency in the current geometry, the near elimination of the fast neutrons will permit them to move the Ge detector and NaI annulus closer to the target without risk of neutron damage to the detector. For the low energy γ rays, a more impressive efficiency gain will come from adding a smaller hyperpure Ge detector much closer to the target.

In summary, the Bi crystal will do two things that are interrelated: it will eliminate the low-energy γ radiation and, thus, lower detection limits for elements with intense low-energy γ rays, and it will reduce the fast neutron flux so that they can move detectors closer to the beam, thus improving their counting efficiencies. Moreover, these changes will improve the precision and accuracy for elements that are now observed if low-energy γ rays are used in the quantitative determination.

A second source of scattered neutrons and γ radiation is the beam stop. They plan to rebuild it to reduce scattered neutrons and better shield out γ rays arising from (n, γ) reactions in the B in the beam stop. The current stop was one of the first components built three years ago and utilizes a large amount of borated polyethylene to absorb fast neutrons. Subsequent experience has indicated that the B content of the polyethylene is too low and that they would have a much more effective stop if they replace it with B_4C in a plastic matrix. They also plan to redesign the lower plate of the beam stop and the entrance hole into the stopping material.

In the area of data analysis, they wish to add a display scope and keyboard to improve the peak-identification and interference-removal methods in their interactive data-analysis procedure. The new data generated by use of the NaI annulus have had a substantial effect on their capacity to identify peaks and determine interferences.

Comments and Recommendations:

This project has made very good progress during its three years of funding. The fourth year should bring the instrumentation to the point that the next renewal could be terminal. This has been discussed with the

principal investigators and they agree that if all goes well two more years should essentially finish the research needed to bring this new analytical tool to the point of use by others. I have discussed the budget with Professor Gordon and he has assured me that they can still install the Bi crystal system although I can't find all of the funds requested. They have requested $112,478. I recommend renewal with $105,000 of new FY 1980 funds. Due to the stated contribution of the university and our continued interest in the use of this analytical tool I also recommend that title to any equipment purchased on this contract be vested in the university.

Walter J. Haubach
Processes & Techniques Branch
Division of Chemical Sciences
Office of Basic Energy Sciences

1079130

RENEWAL PROPOSAL

TO

THE DIVISION OF BASIC ENERGY SCIENCES
U. S. DEPARTMENT OF ENERGY

"NON-DESTRUCTIVE DETERMINATION OF TRACE ELEMENT CONCENTRATIONS"

SUBMITTED BY

Glen E. Gordon, Professor of Chemistry, [redacted] Phone 301-454-4422

William H. Zoller, Associate Professor of Chemistry, [redacted]
Phone 301-454-4421

William B. Walters, Professor of Chemistry, [redacted] Phone 301-454-4421

Department of Chemistry
University of Maryland
College Park, Maryland 20742

Funds requested: $112,478.00

Contract period: November 1, 1979 - October 31, 1980

Present Contract No.: EY-76-S-05-5173

1079131

SIGNATURE PAGE

The University of Maryland will accept and administer a grant awarded to it under the terms of this proposal.

The University of Maryland is an educational institution in the State of Maryland and retains more than 500 employees.

The bidder represents that he has not employed or retained a company or person (other than a full-time employee) to solicit or secure this grant, and agrees to furnish information thereto as requested by the Contracting Officer.

The University of Maryland certifies that the distributions of costs between the direct and indirect categories as shown in the proposal conforms to the usual accounting practices of the institution for all federally supported or sponsored research.

Glen E. Gordon
Professor
Department of Chemistry

William H. Zoller
Associate Professor
Department of Chemistry

William B. Walters
Professor
Department of Chemistry

James R. McNesby
Professor and Chairman
Department of Chemistry

Francis Stark, Jr.
Provost
Division of Agricultural
and Life Sciences
University of Maryland

Robert L. Gluckstern
Chancellor
College Park Campus
University of Maryland

1079132

I. INTRODUCTION

As detailed in our 1979 Progress Report [ORO-5173-003], our principal accomplishments during the past year can be broken down into several categories:

- °Data collection - Compton suppressor and pair spectrometer were brought into operation and tested.
- °Data analysis - Modified interactive programs for use with pair and Compton-suppression modes.
- °Tests of accuracy and Precision - Determined compositions of many National Bureau of Standards (NBS) Standard Reference Materials (SRM), obtaining excellent agreement with NBS values and other reported measurements; performed analyses for several elements not yet certified by NBS.
- °Applications to Additional Types of Samples - Measured concentrations of many elements in a wide range of U. S. Geological Survey (USGS) standard rocks plus a number of samples from Antarctica.
- °Isotopic Ratios - We have begun to explore the possibilities of using neutron-capture prompt γ-ray activation analysis (PGAA) for detecting differences in isotope ratios of elements such as Si, Fe and Mg in rocks, minerals and biological samples and the possibility of detecting stable isotope tracers in medical studies.

1079133

During the coming year, we propose to focus our efforts on reducing backgrounds and increasing sensitivities for observation of various γ rays, especially at low energies. With these improvements we hope to be able to lower detection limits for elements now observable and to extend the PGAA method to additional elements. We also plan to extend the analytical studies to new classes of samples, with emphasis on samples relevant to energy sources. In addition, we plan to upgrade our data handling capabilities.

II. PROPOSED SYSTEM CHANGES

The limits of detectability for elements with major γ-ray transitions below 400 keV are large because of the presence of a large quantity of γ radiation scattered from the beam by the target itself (see Fig. 1). As this radiation originates at the target, the Compton suppression system does not reduce it significantly. Over 99.9% of this γ radiation can be eliminated by placing an oriented single crystal of very highly purified Bi cooled to liquid nitrogen temperature in the beam. Moreover, 94% of the fast neutrons can also be eliminated while the flux of thermal neutrons would be reduced by only 50%.

The reduction of the low energy background would lower the limits of detectability for a number of important elements. In our original proposal for this project, we calculated the count rates expected for the most intense γ ray of each element during irradiation of 10g of average crustal meterial. We reproduce a portion of that table in Table 1. Our calculations were quite reliable, as we have been able to observe all but two of the first 17 on the list in crustal type samples (USGS) rocks and NBS fly ash), plus the 28th element, V. Note that the unobserved elements among the top 17, Eu and Sc, have their most intense predicted peaks at 329 and 229 keV, repectively. The latter may be impossible to observe because of the peak from Fe and Sm at 230.2 keV, but the former might well become

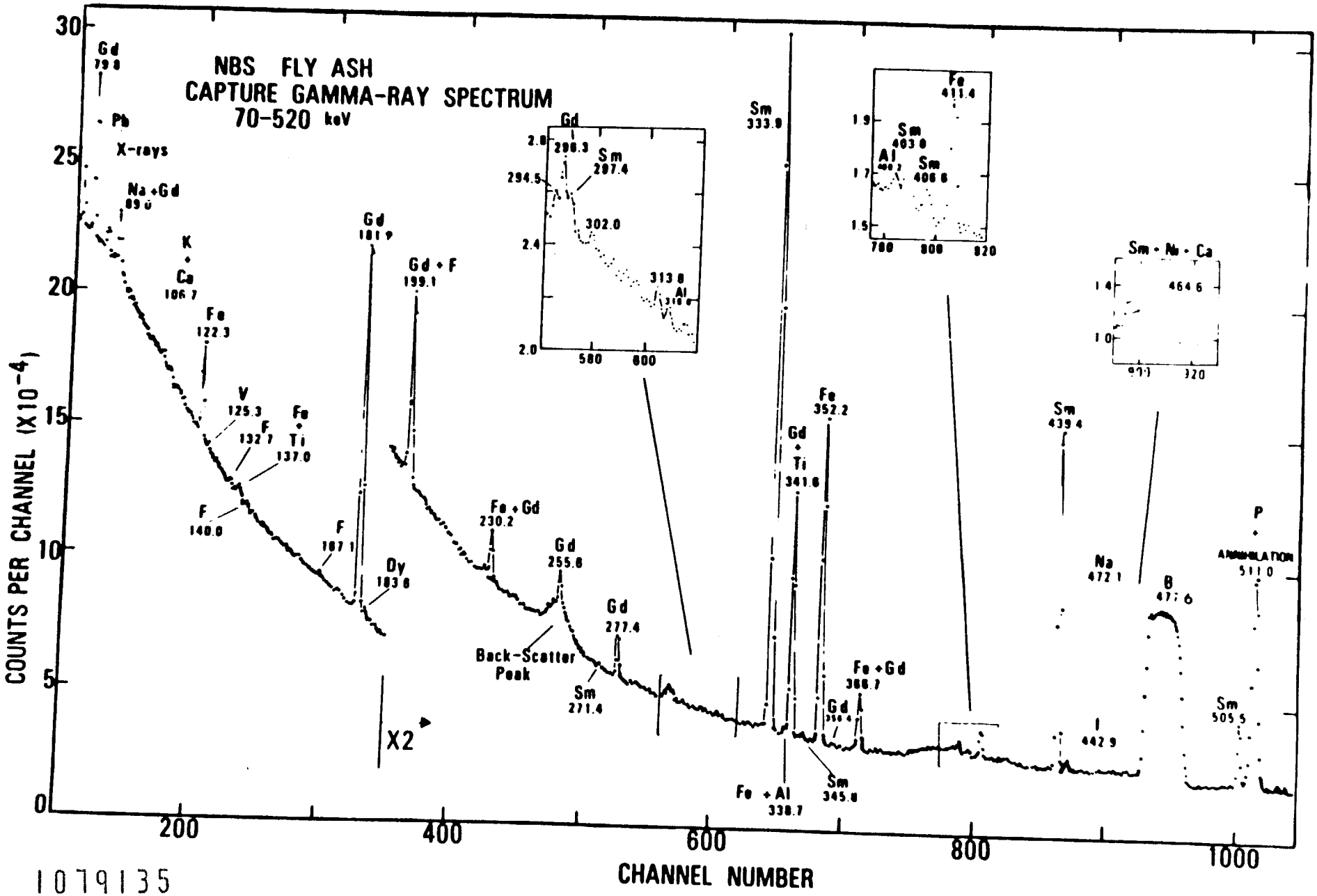
NBS FLY ASH
CAPTURE GAMMA-RAY SPECTRUM
70-520 keV
COUNTS PER CHANNEL (X10^{-4})
CHANNEL NUMBER
Gd 79.8
Pb X-rays
Na+Gd 89.0
K + Ca 106.7
Fe 122.3
V 125.3
F 132.7
Fe + Ti 137.0
F 140.0
F 187.1
Gd 181.9
Dy 183.8
Gd + F 199.1
Fe + Gd 230.2
Gd 255.8
Back-Scatter Peak
Sm 271.4
Gd 277.4
X2
Sm 333.9
Gd + Ti 341.8
Fe + Al 338.7
Sm 345.8
Fe 352.2
Gd 356.4
Fe + Gd 366.7
Sm 439.4
I 442.9
Na 472.1
B 477.6
Sm 505.5
P + ANNIHILATION 511.0
Gd 296.3
Sm 297.4
294.5
302.0
313.8
Al
Fe 411.4
Sm 403.8
Al
Sm 406.8
Sm + Na + Ca
464.6
1079135

Table 1. Elements Predicted to be Observable in PGAA of Crustal Material Compared with Actual Observed Elements

lement	Crustal[a] Abundance (ppm)	Predicted Count Rate (c/sec)	Observed ? or Predicted E_γ (keV)	Element	Crustal[a] Abundance (ppm)	Predicted Count Rate (c/sec)	Observed ? or Predicted E_γ (keV)
Gd	8	264	Yes	Zn	60	0.28	No: 1077
Sm	6	104	Yes	Sr	290	0.2	No: 1836
K	28,200	100	Yes	La	44	0.2	No: 220
Si	305,400	90	Yes	Cr	70	0.19	No: 835
Fe	35,400	53	Yes	Ni	44	0.17	No: 465
Ti	4,700	50	Yes	V	95	0.14	Yes
Al	78,300	38	Yes	Nb	20	0.07	No: 191
Na	24,500	30	Yes	Ta	3.4	0.07	No: 271
Eu	1.4	23	No: 329	Y	34	0.044	No: 6080
Ca	28,700	14	Yes	Pr	8	0.035	No: 178
Mn	690	7	Yes	Tb	1	0.03	No: 597
B	10	4	Yes	Ce	75	0.02	No: 662
Sc	14	1.9	No: 229	Zr	160	0.02	No: 934
Cl	320	1.9	Yes	Br	2.9	0.02	No: 246
Nd	25	1.6	Yes	Hg	0.03	0.02	No: 372
S	310	1.1	Yes	Tm	0.5	0.016	No: 238
Cd	0.1	0.8	Yes	Lu	0.6	0.015	No: 458
Dy	6	0.7	No: 538	Ag	0.06	0.014	No: 200
Hf	3	0.65	No: 214	Ho	1.2	0.012	No: 240
P	1,050	0.63	Marginal	Ga	17	0.005	No: 2202
Cu	30	0.3	No: 278	Cs	3	0.005	No: 308
Co	12	0.28	No: 556	In	0.07	0.0025	No: 273

alculated for a 10-g sample of crustal material in a flux of 10^9 n/cm^2-sec observed with a 15% efficient Ge(Li) detector
) cm from the sample.

107913b

observable if the background at 329 keV were reduced. Also, note that the most intense peaks for many elements further down the list fall below 400 keV. Thus, if we could greatly reduce the background in this region, we could possibly measure concentrations of many of these elements. It must be noted, however, that some of the lines listed may fall under other intense peaks, as in the example of the Eu line noted above. On the other hand, the most intense peak is usually not the only peak observable and often it is not the best one for measurements, as a less intense peak may fall in a cleaner area of the spectrum. Thus, the list on Table 1 is only an indication of what might be possible, not a guarantee.

Two important elements not listed in the original proposal were U and Th, for which no data were given in Rasmussen's compilation of capture spectra (because of complications caused by fission-products lines?). Both elements will have low-energy capture lines and we have had unconfirmed indications of U lines in spectra taken with our present set-up. Thus, these elements may also become observable.

From recent studies of the capture gamma-ray spectra of Th and U, we can see that we will be about 10 times more sensitive to U than to Th. In the $^{238}U\ (n,\gamma)$ reaction (M. R. Schniorak, Nucl. Data Sheets 21, 153, 1977), the 133.8-keV gamma ray has an intensity of 23/100 n captures, whereas in Th there are no strong γ rays, only several low energy lines (e.g., 256, 319, 336 keV) with intensities of 1.5/100 and Fe high energy lines with intensities greater than 1/100 (Y. A. Ellis, Nucl. Data Sheets 24, 289, 1978).

The list of Table 1 is for the crustal abundance pattern. One would, of course, get quite a different order of elements for biological, marine or other types of samples . However, reduction of the low energy background should reduce detection limits for a number of elements in these types of samples, too.

1079137

Although the loss of 50% of the neutrons will reduce the efficiency in our current geometry, the near elimination of the fast neutrons will permit us to move the large (>20%) Ge detector and NaI annulus closer to the target without risk of neutron damage to the detector. For the low energy rays, a more impressive efficiency gain will come from adding a smaller (10%) hyperpure Ge detection much closer to the target.

In summary, the Bi crystal will do two things that are interrelated: it will eliminate the low-energy γ radiation and, thus, lower detection limits for elements with intense low-energy γ rays, and it will reduce the fast neutron flux so that we can move detectors closer to the beam, thus improving their counting efficiencies. Moreover, these changes will improve the precision and accuracy for elements that we now observe if low-energy γ rays are used in the quantitative determination.

A second source of scattered neutrons and γ radiation is the beam stop. We wish to rebuild it to reduce scattered neutrons and better shield out rays arising from (n,γ) reactions in the B in the beam stop. The current stop was one of the first components built three years ago and utilizes a large amount of borated polyethylene to absorb fast neturons. Subsequent experience has indicted that the B content of the polyethylene is too low and that we would have a much more effective stop if we would replace it with B_4C in a plastic matrix. We also need to redesign the lower plate of the beam stop and the entrance hole into the stopping material.

These two improvements should reduce both neutron and γ-ray backgrounds and substantially improve the detection limits for elements with major γ rays with energies below 400 keV. It should be noted that the latter improvement is needed even if we make the former. The Bi crystal should improve our Cd ratio from 55/1 to about 1000/1. With a flux of ~10^8 n/cm^2/sec, this still leaves a formidable 10^5 fast neutrons/cm^2/sec to be handled in the beam stop.

1079138

In the area of data analysis, we wish to add a display scope and keyboard to improve the peak-identification and interference-removal methods in our interactive data-analysis procedure. The new data generated by use of the NaI annulus have had a substantial effect on our capacity to identify peaks and determine interferences. We can presently display only one spectrum or portions thereof at one time. In Fig. 2 we show the same energy range for the singles, pair and Compton-suppressed, or "full energy", spectra. We use the term "full energy" as the suppression requirements eliminates more than just Compton processes, but also greatly reduces the single-and double-escape peaks. Thus, the full-energy peaks are greatly enhanced relative to other features of the spectrum. On the other hand, the pair requirements appear to almost completely eliminate full-energy peaks and greatly reduce single-escape peaks. By viewing these three spectra together, clear peak identification is easily made and interference levels readily determined. Such a capability is particularly important as we explore the analysis of new types of samples and try to determine the accuracy and precision that can be achieved for the elements in each of them.

III. NEW TYPES OF SAMPLES

During the next year, we will investigate the application of PGAA to several additional classes of samples. The technique has already shown itself to be a useful complement to INAA and other methods in the analysis of coal, fly ash and rocks, in which about 17 elements can usually be measured reliably. One point that we did not fully appreciate before testing the PGAA method is that it is capable of yielding very high accuracies for elements with strong peaks. The reasons for this are:

1079139

1. samples can be irradiated for very long periods to build up good statistics (and we've often run 20-hr spectra when characterizing standards);
2. for many elements, there are at least five strong lines upon which to base and cross-check the analysis; and
3. there are no appreciable dead-time factor changes with time or other timing errors of the sort that contribute to overall error in INAA measurements of elements with short-lived products.

Because of the demonstrated accuracy and reliability of PGAA, the Activation Analysis Section at NBS is beginning to use the method in their certification procedures for new SRMs.

Below is a brief outline of the types of samples that will be studied by PGAA.

A. Energy Related Samples

The value of PGAA as applied to coal and fly ash has been demonstrated, although additional elements may become measurable with the improvements proposed in Sect. II. Note that these detailed studies of the prompt γ-ray spectra should be of value to groups at the National Laboratories who are developing real-time methods (based on ^{252}Cf) for analysis of product streams in fossil-fuel reatment plants.

During the next year, we will focus more on the analysis of petroleum-related samples: Crude oil and its distilled and residual fractions, oil shale, tar sand, etc. We will begin by study of NBS standard residual oil (SRM 1634), which has proven to be much more difficult to analyze by conventional methods than coal and fly ash. We already have a number of crude oils from oil companies and, in some cases, the various fractions from those crudes. We will also have an opportunity to run some very low boiling fractions such as gasoline, which can be placed inside a reactor only under very carefully controlled conditions, but which should present little problem in the external beam.

1079140

We have been contacted by a staff member from Battelle Northwest Laboratory in regard to running some oil shales and plan to do so soon. It should be noted that our investigations of these types of samples should not only be of value to other groups doing similar work in laboratories, but may also be valuable in field studies, e.g., logging of bore holes in oil shale with portable neutron sources. One should also keep in mind the fact that PGAA is sensitive not only to the mineral portions of samples of these types, but can also measure the "organic" elements such as C, H, N and S, which may be quite useful. For example, the H/C ratios of petroleum substances are important as an indicator of the aromatic-to-aliphatic ratio. (Of course, one has to have the sample free of water or know the water content to remove the hydrogen contribution by water.) Also, S and N are important in regard to the air pollution problems that would be associated with use of a fuel.

B. High Purity Materials

We have just begun to explore the use of PGAA in studies of high purity materials of importance in electronics, communications and solar energy conversion. The properties of such materials are, of course, strongly influenced by the impurities present. The limits of detection required in many of these problems (e.g., for B in high purity Si) are considerably lower than the limits we reported for coal and bovine liver in our major paper on PGAA. However, that does not preclude the possiblity for these applications, because high purity materials will have such low concentrations of many elements with high cross sections that the spectra should have many fewer strong lines and a lower general background than for more complex natural materials. Thus, if the matrix material itself is not strongly activated, as in the case of Si, the limits of detectability may be decreased by orders of magnitude. It would be very valuable in the industry to have a rapid,

1079141

non-destructive technique such as PGAA available so that results to analyses could be obtained during batch operations, allowing one to modify the process if the product was not going to meet specifications.

C. Biological Samples

As we learn more about trace elements in biological systems, in human beings in particular, the more we appreciate the fact that their importance for good health is many orders of magnitude greater than their minute concentrations would imply. Progress in this field has been limited by the analytical methods available. Methods currently in use require laborious ashing and chemical preparation of samples. Some require large sample size in order to obtain enough of the trace element to see a signal. Even INAA, which has been extremely useful for measuring trace elements in crustal samples, has had severe problems with biological samples, mainly because of the enormous amounts of ^{24}Na, ^{38}Cl and ^{42}K produced during irradiations, which obscure most other activation products with half lives less than a few days.

During the next year, we plan to focus more attention on the analysis of biological samples. Until now, we have tested PGAA of biological samples only by analysis of NBS Orchard Leaves and Bovine Liver standards. The results obtained were mixed: a dozen or so elements could be measured quite reliably, but the number observable was smaller than for more crustal type samples. However, some of the elements observed are quite important. As we can measure both C and N reliably, we can obtain C/N ratios, a tradiational measure of the protein content of biological samples. Boron and Cd are important trace elements, the latter because of its toxicity.

Despite the small number of elements so far observed by PGAA, we feel that much more can be done, especially in view of the improvements proposed in Sect. II.

1079142

Therefore, we propose to investigate the use of PGAA with a wide range of biological samples: blood, serum, teeth, bones, hair, urine, saliva and, possibly, organs from the specimen bank being established at NBS. Much of the above work will be done in collaboration with Dr. Robert I. Henkin (M.D. and Ph.D.) from Georgetown University Medical Center, a world expert on medical aspects of trace elements (and chariman of the NAS/NRC Committee that recently produced the definitive report on the role of Zn in the body). Already we have collaborated with him on the study of trace elements in freeze-dried saliva with the use of INAA and IPAA. We are now designing a project to investigate the possible role of trace elements in saliva in periodontal disease and tooth decay (not to be funded by DOE).

Somewhat further in the future, we want to explore in more depth the possibilities for using stable isotope tracers in humans by detecting changes in isotope ratios with PGAA. As described in the Progress Report, the calculations by Dr. Roy indicate that the use of PGAA for stable isotope tracing in the body would be limited to about five elements and, because of the large amounts of enriched isotopes required, the cost per test would be a minimum of about $1000.

Despite the rather grim assessment of the possibilities for stable isotope tracing, we don't feel that the effort should be abandoned. The need for such a method is enormous. Much of our present knowledge of the behavior of trace elements in the body has been determined by following the distributions of injected or ingested radioactive tracers. Indeed thousands of <u>routine</u> diagnostic tests are performed daily throughout the U.S. by the use of ^{131}I, ^{99}Tc and many other tracers. However, as pointed out to us by Dr. Henkin, radioactive tracers cannot be used in research on persons below the age of 18 nor in pregnant women. This means that some of the most important human trace element problems are excluded from study, namely, the role of trace elements during the development of fetuses

1079143

and in children up to and through the age puberty. Thus, there is a high priority in medical and nutritional fields for development of alternate methods. Even at the high price per experiment noted above, there might be some experiments that would be worth the price. Some improvements may be possible after our proposed experiments to improve our ability to detect elements in biological samples by PGAA. Also, it should be noted that Dr. Roy's calculations were for the use of PGAA aone. It would be inherently most accurate to observe changes of isotope ratios simply from the ratios of areas of two or more different peaks in the same spectrum, as in PGAA. However, if the sensitivity for that is not great enough there are other approaches. For example, one might observe one isotope via PGAA and another via INAA or IPAA. Already there are several cases in INAA and IPAA in which irradiation products of two different isotopes are seen following irradiation of certain kinds of samples: e.g., 244-day ^{65}Zn and 14-hr ^{69m}Zn, 83-min ^{139}Ba and 12-day ^{131}Ba in INAA and 52-hr ^{203}Pb and 67-min ^{204m}Pb in IPAA. The use of two separate methods would require very careful intercalibration of the methods, but this would not be impossible. Although it would add greatly to the amount of labor per sample, enormous improvements in sensitivity could be made by doing some chemical separations, e.g., removal of Na, Cl and K prior to analysis. Furthermore, all of Roy's calculations were based on blood, whereas there are other types of samples from the body (spleen, kidney, liver, saliva) where some elements may be so strongly enriched as to make there analysis much easier.

In summary, although our analytical capabilities for analysis of human samples are now quite primitive, the possibilities are quite exciting and the pay-off, if successful, would be enormous.

IV. LIBRARY DEVELOPMENT

We are slowly developing a library of standard capture gamma-ray spectra of

1079144

pure materials. We are, of course, indebted to work by physicists for the literature data, but their targets are generally chosen for the nuclear structure information to be obtained. By necessity we are developing a library of standard spectra of elements present in samples such as coal, fly ash, atmospheric particulate matter, volcanic emissions, etc. We expect to continue this activity during the coming year. Already we are publishing a substantial amount of information on the energies, intensities and interferences for most lines that are useful for analyses of elements in our major paper on PGAA. At some stage in the future it may be desirable to publish a compilation of all of the γ-ray energies and intensities for the standards we have investigated.

1079145

IV. PROPOSED BUDGET

Non-Destructive Determination of Trace Element Concentrations

Renewal of Contract No. EY-76S-06-5173 with the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy for the period November 1, 1979 -October 31, 1980

		Requested from DOE	Univ. of Md. Contribution
A. Salaries and Wages			
1. Principal Investigators			
G. E. Gordon (10% of academic year)			$ 3450.00
W. B. Walters (5% of academic year)			1287.00
W. H. Zoller (10% of academic year) (5% of summer)		$ 3154.00	2490.00
		$ 3154.00	$ 7227.00
2. Research Associate			
Dr. D. L. Anderson (100%)		$ 17000.00	
3. Graduate Student		7000.00	
4. Undergraduate Assistants (hourly help)		3000.00	
Total Salaries and Wages		$ 30154.00	$ 7227.00
B. Permanent Equipment			
1. Beam Stop Reconstruction	$ 2000		
2. Filter Assembly with Cooled Bi Crystal	15000		
3. Data Processing Terminal	10000		
Total Permanent Equipment		$ 27000.00	
C. Expendable Supplies		$ 6500.00	

1079146

D. Other Expenses			
1. Repair and Maintenance	$ 3500		
2. Reactor fee (NBS Contract plus Liquid N_2)	10000		
Total Other Expenses		$ 13500.00	
E. Travel (domestic)		4500.00	
F. Publications and Communications		3500.00	
G. Fringe Benefits		4242.00	$ 1134.00
H. Total Direct Costs		$ 89396.00	$ 8361.00
I. Overhead			
1. 41% of TDC less Items B and D.2			
0.41 x 52,396 = $21482			3428.00
2. 16% of Item D.2 (off campus)			
0.16 x 10,000 = $1600			
Total Overhead		$ 23082.00	
J. Total Costs		$112478.00	$ 11789.00

1079147

VI. COMMENTS ON THE BUDGET

A. Personnel

The budget reflects only the personnel costs to DOE or the University of Maryland. In addition to the personnel listed, we will have two other workers at no cost to the project: Dr. Richard Lindstrom of the Center for Analytical Chemistry, NBS has been spending a portion of his time working with us on the project under support of NBS. This was a commitment made by NBS when this project was initiated. Although NBS does not formally appear as a part of the proposal (except for charges for use of the reactor), this is a joint effort with them and personnnel from the Center for Analytical Chemistry and from the Reactor Staff have been most helpful to us throughout the work, especially the Control Room Staff. Secondly, Prof. Namik Aras of the Middle East Technical University, who is highly experienced in the use of radioactivity will be spending a leave with us as a Visiting Professor of Analytical Chemistry during the coming academic year and has expressed his desire to participate in this project.

B. Equipment

1. The beam stop was one of the first pieces of the system constructed in 1977 as it has to be in place before we could run. The design used has proven satisfactory as it permits us to take data and carry out the many tests descsribed in the two progress reports. Nonetheless, it is neither ideal nor optimum. Our experience has shown that we can do better, especially with respect to reducing neutrons scattered back towards the detector. The funds requested will be used to add B_4C in a plastic matrix to the stop in place of the borated polyethylene and to rework the bottom plate of the assembly to aid in the reduction of neutron backscatter.

2. The installation of the cooled Bi crystal will necessitate considerable changes in the lower portion of the beam line and substantial additional shielding.

1079148

Although the Bi absorbs the rays, it merely scatters the fast neutrons out of the beam. Thus, sizeable quantities of B_4C are required to absorb the scattered fast neutrons and this must be surrounded by Pb to contain the 478-keV γ ray from the $^{10}B(n,)^7Li$ reaction. We estimate that the $15,000 expenditure will be distributed as follows: $2000 for the crystal itself, $4000 for the cryogenic mounting, $5000 for the B_4C and Pb shielding and their mounting and installation, and $4000 for alterations in the beam line to accommodate all of these changes (and those of Item 1).

3. The provision of the enhanced interactive data reduction terminal will be accomplished by acquiring a keyboard and display scope, an interface to the computer, and the necessary basic software for the operation of the scope. We hope to acquire these as a package, but estimate that the scope will comprise ~$7000, the interface ~$1000 and the software, ~$2000.

C. Expendable Supplies

The expendable materials include significant expenditures for high purity materials for standards, preparative materials, magnetic tape, disc packs for the data system, as well as many smaller items consumed in the course of the work.

D. Other Expenses

1. Repair and Maintenance

We now have over $150,000 in capital equipment including the data collection and processing system and the γ-ray spectrometer system. As most of these components are out of warranty, these funds will be used for repair and maintenance to keep our system functioning.

1079149

2. Reactor Charges

This item has been increased to reflect increased reactor operating expenses and the charges for liquid nitrogen which are included here. By purchasing LN_2 here rather than carrying it from the University, an occasional trip is eliminated.

E. Travel

The large increase here is a reflection of the costs involved in travel to NBS to do experiments plus travel to conferences and meetings. In addition to the increase in gasoline costs, the University's motor pool has now levied a $3.00 per day charge in addition to mileage and gasoline charges. We estimate we will make 5 trips per week for 50 weeks totalling 250 trips at a cost of approximatly $12 per trip.

F. Publications and Communciations

Included in this item are funds for drafting of figures, long distance telephone calls, the cost of the annual progress report, copying of articles, rental of word processing equipment, and page charges for journal articles.

G. Fringe Benefits

The fringe benefits are calculated on the basis of 6.13% social security, 6.13% state retirement system, 0.57% unemployment compensation, and $828/year for hospitalization per academic staff member. For graduate students, only the hospitalization is included and nothing is included for the hourly undergraduate employees.

I. Overhead

We are pleased to point out the overhead rate reduction from 48% to 41% of modified total direct costs for on-campus work and from 17% to 16% for off-campus work.

1079150

VII. OTHER SOURCES OF RESEARCH SUPPORT

A. Existing Contracts and Grants

W. B. Walters

Radioactive Decay Studies at TRISTAN II, DOE Contract DE-AS05-79ER10494, $108,124, July 1, 1979 - June 30, 1980, 20% academic year, 2 months summer.

University of Maryland Cyclotron, NSF Grant PHY-78-20749, $987,000 (with an extension approved through June 30, 1980 for ~$500,000), January 1, 1979 - December 31, 1979 (with D. L. Hendrie, H. D. Holmgren, P. G. Roos, N. S. Wall, N. S. Chant, C. C. Chang, H. Breuer and V. E. Viola), 20% time.

Non-Destructive Determination of Trace Element Concentrations, DOE Contract DE-AS05-76ERO 5173 M003, $81,101, November 1, 1978 - October 31, 1979 (with G. E. Gordon and W. H. Zoller), 10% time.

G. E. Gordon

Non-Destructive Determination of Trace Element Concentrations, DOE Contract DE-AS05-76ERO 5173 M003, $81,101, November 1, 1978 - October 31, 1979 (with W. B. Walters and W. H. Zoller), 10% time.

Sources, Transformation and Speciation of Atmospheric Pollutants, NSF Contract PFR 75-02667806, $49,024, March 1, 1979 - February 29, 1980 (with W. H. Zoller), 5% time.

Interpretation of the RAPS Atmosphric Elemental Concentration Data, EPA Contract R806263-01-1, $56,224, September 1, 1978 to November 15, 1979, 10% academic year, 1 month summer.

W. H. Zoller

Sources, Transformation and Speciation of Atmospheric Pollutants, NSF Contract PFR 75-02667806, $49,024, March 1, 1979 - February 29, 1980 (with G. E. Gordon), 5% time.

Non-destructive Determination of Trace Element Concentrations, DOE Contract DE-AS05-76ERO 5173 M003, $81,101, November 1, 1978 - October 31, 1979 (with W. B. Walters and G. E. Gordon).

Effect of Power Plants on Macromolecular Organic Matter in Estuaries, State of Maryland Power Plant Siting Program Contract P-497804, $98,453, January 1, 1978 - December 30, 1979 (with G. Helz), 5% time.

Sources and Distributions of Trace Elements in the Antaractic Atmosphere, NSF, $49,000, August 1, 1979 - July 31, 1981 (with R. Duce), 10% time.

1079151

The Fate of Mercury Released from Power Plants, Power Plant Siting Program of the State of Maryland Contract P51-79-04, $48,738, October 15, 1978 - October 14, 1979, 10% time.

The Composition of Remote Area Aerosols from Antarctica and Hawaii, NOAA (GMCC Program), Contract #NA79-RAC00050, $62,387, February 1, 1979 -January 30, 1980,10% time.

1079152

VIII. FINANCIAL STATEMENT

1.	Total actual project cost to date for the current period	$ 375,310
2.	Estimated total cost for remainder of period	18,114
3.	Total actual and estimated cost chargeable to DOE for current period based on percentage of cost agreed upon as contained in A-III of Appendix "A" to Contract	393,424
4.	Accumulated costs chargeable to DOE (incude costs reported in certified statement for preceding period(s) and the costs staed in Item 3 above)	393,424
5.	Accumulated DOE Support Ceiling as stated in Article III of Contract	393,424
6.	Total estimated DOE funds remaining under Contract subtract Item 4 from 5 which may be used to reduce amount of new funds required from DOE for proposed period	0

1079153

ASSURANCE OF COMPLIANCE WITH THE ENERGY RESEARCH
AND DEVELOPMENT REGULATION UNDER
TITLE VI OF THE CIVIL RIGHTS ACT OF 1964

University of Maryland, College Park (hereinafter called the "Applicant") HEREBY AGREES THAT it will comply with title VI of the Civil Rights Act of 1964 (P. L. 88-352) and all requirements imposed by or pursuant to the Regulation of the Department of Energy (10 CFR Part 4) issued pursuant to that title, to the end that, in accordance with title VI of that Act and the Regulation, no person in the United States shall, on the ground of race, color, or national origin, be excluded from participation in, be denied the benefits of, or be other wise subjected to discrimination under any program or activity for which the Applicant receives Federal financial assistance from the Department of Energy; and HEREBY GIVES ASSURANCE THAT it will immediately take any measures necessary to effectuate this agreement.

If any real property or structure thereon is provided or improved with the aid of Federal financial assistance extended to the Applicant by the Department of Energy, this assurance shall obligate the applicant, or in the case of any transfer of such property, any transferee, for the period during which the real property or structure is used for a purpose for which the Federal financial assistance is extended or for another purpose involving the provision of similar services or benefits. If any personal property is so provided, this assurance shall obligate the Applicant for the period during which it retains ownership or possession of the property. In all other cases, this assurance shall obligate the Applicant for the period during which the Federal financial assistance is extended to it by the Department of Energy.

THIS ASSURANCE is given consideration of and for the purpose of obtaining any and all Federal grants, loans, contracts, property, discounts, or other Federal financial assistance extended after the date hereof to the applicant by the Department of Energy including installment payments after such date on account of applications for Federal financial assistance which were approved before such date. The Applicant recognizes and agrees that such Federal financial assistance will be extended in reliance on the representations and agreements made in this assurance, and that the United States shall have the right to seek judicial enforcement of this assurancea. This assurance is binding on the Applicant, its successors, transferes, and assignees, and the person or persons whose signatures appear below are authorized to sign this assurance on behalf of the Applicant.

Date_____ University of Maryland, College Park

By_____

Robert Gluckstern, Chancellor
College Park Campus
College Park, Maryland 20742

1079154

DOE F 1325.8
(7-79)

U.S. DEPARTMENT OF ENERGY

memorandum

DATE SEP 30 1980

REPLY TO ATTN OF ER-162

SUBJECT Justification for Acceptance of a Renewal Proposal from the University of Maryland (Gordon, Zoller & Walters) for Contract No. DE-AS05-76ER05173

TO James S. Kane, ER-10

Title:

"Non-Destructive Determination of Trace-Element Concentrations"

Scope:

The application of neutron-capture prompt gamma-ray analysis for the determination of trace elements which are not determinable by neutron activation.

Recent Progress:

They continued to investigate the application of prompt gamma activation analysis (PGAA) to several new types of samples. It is especially useful for crustal samples since it not only determines the trace elements it determines the major ones also. Using the common geochemical technique of expressing the masses of major elements as their oxides they typically account for 95 to 100% of the sample mass. This was especially demonstrated this year on measurements of Mt. St. Helens ash and other volcanic samples. Despite this good agreement they still are dubious about using the common oxide basis and plan to develop a method for oxygen measurements next year.

During the past year they began studies of oil shales, shale oil and oil. The oil shales can be analyzed for about the same elements as done last year for coal and fly ash but the shale oil and other oils are more difficult and require further work. Two other areas look promising; biological samples and the analysis of high purity material for trace constituents.

Last year Mike Failey received his Ph.D. and his thesis contains a detailed table of the best γ rays to use for the analysis of various elements and their expected interferences.

Even more progress would have been made, however, the NBS reactor was shut down from September, 1979, to March, 1980, due to problems with shim-rod controls. Also the supplier of the data acquisition equipment for upgrading went bankrupt before completing the work.

1079155

Publications:

1. M. P. Failey, D. L. Anderson, W. H. Zoller, G. E. Gordon and R. M. Lindstrom, "Neutron Capture Prompt γ-Ray Activation Analysis for Multi-Element Determination in Complex Samples," Anal. Chem. 51, 2209-2221 (1979).

2. M. S. Germani, I. Gokmen, A. C. Sigleo, G. S. Kowalczyk, I. Olmez, A. Small, D. L. Anderson, M. P. Failey, M. C. Gulovali, C. E. Choquette, E. A. Lepel, G. E. Gordon and W. H. Zoller, "Concentrations of Elements in the National Bureau of Standards Bituminous and Subbituminous Coal Standard Reference Materials," Anal. Chem. 52, 240-245 (1980).

Three additional papers are in press and another has been submitted for publication.

Proposed Research:

Due to the reactor and data handling problems last year some of the proposed research was not accomplished. This year they plan to catch up with their plans to install the cryogenics and single bismuth crystals in the beam, addition of a second Ge detector, and completion of the analysis of a number of geological, energy-related, and high-purity samples (like B in Si semiconductors).

They also plan to apply PGAA using isotopic sources of neutrons which are portable and in particular plan to investigate ways to determine oxygen using low energy neutrons. One involves the use of the $^{18}O(n,\gamma)^{19}O$ reaction that yields 27 sec. ^{19}O. The cross section is quite small but the large amounts of oxygen usually present and the high specific activity of the short-lived species may make it feasible.

Comments and Recommendations:

During the past year the tremendous capabilities of neutron-capture prompt γ-ray activation analysis became apparent to a much wider community of potential users. Prior to this year the Maryland group and a group at LANSL were the only groups in the U.S. with a major involvement in development of reactor-based PGAA. This year a third group at the University of Missouri reactor finished construction of a system and began major experiments.

They anticipate funding from the USDA Human Nutrition Program for the development of stable-isotope tracers for use in humans and have received funding from NASA for studies of the atmospheric emissions from volcanoes. Graduate students will conduct these studies using the PGAA system assembled on this contract. An excellent case of short term spin-off activities.

1079156

This is a productive contract and I recommend renewal with $95,000 of new FY 1981 funds. Due to the stated contribution I also recommend that title to any equipment purchased on this contract be vested in the university.

Walter J. Haubach
Processes & Techniques Branch
Division of Chemical Sciences
Office of Basic Energy Sciences

1079157

RENEWAL PROPOSAL

TO

THE DIVISION OF BASIC ENERGY SCIENCES
U. S. DEPARTMENT OF ENERGY

"NON-DESTRUCTIVE DETERMINATION OF TRACE ELEMENT CONCENTRATIONS"

SUBMITTED BY

Glen E. Gordon, Professor of Chemistry, [redacted] Phone 301-454-4422

William H. Zoller, Associate Professor of Chemistry, [redacted]
Phone 301-454-4421

William B. Walters, Professor of Chemistry, [redacted] Phone 301-454-4421

David L. Anderson, Research Associate, [redacted] Phone 301-454-4421

Department of Chemistry
University of Maryland
College Park, Maryland 20742

Funds requested: $105,135

Contract period: November 1, 1980 - October 31, 1981

Present Contract No.: DE-AS05-76ER05173

1079158

SIGNATURE PAGE

The University of Maryland will accept and administer a grant awarded to it under the terms of this proposal.

The University of Maryland is an educational institution in the State of Maryland and retains more than 500 employees.

The bidder represents that he has not employed or retained a company or person (other than a full-time employee) to solicit or secure this grant, and agrees to furnish information thereto as requested by the Contracting Officer.

The University of Maryland certifies that the distributions of costs be tween the direct and indirect categories as shown in the proposal conforms to the usual accounting practices of the institution for all federally supported or sponsored research.

Glen E. Gordon
Professor
Department of Chemistry

William H. Zoller
Associate Professor
Department of Chemistry

William B. Walters
Professor
Department of Chemistry

David L. Anderson
Research Associate
Department of Chemistry

Paul H. Mazzocchi
Professor and Acting Chairman
Department of Chemistry

Larry Vanderhoef
Provost
Division of Agricultural
and Life Sciences
University of Maryland

Robert L. Gluckstern
Chancellor
College Park Campus
University of Maryland

1079159

I. INTRODUCTION

As described in the accompanying 1980 Progress Report, the technique of neutron-capture prompt γ-ray activation analysis (PGAA) has been established as a useful analytical method for application to a wide range of materials, especially to crustal and energy-related samples such as coal, fly ash, oil shale and rocks. These advances are being made at several laboratories, as the interest in development and use of PGAA has grown. Major milestones from our laboratory include two major papers published in Analytical Chemistry, one of which described the PGAA method as applied to the analysis of several National Bureau of Standards (NBS) Standard Reference Materials (SRMs): three coals, two fly ashes and two botanical standards (1). In the second paper (2), PGAA was used in conjunction with other nuclear methods to determine concentrations of 51 and 43 elements in the new NBS standard eastern and western coals (SRM 1632a and 1635, respectively).

During the past year, we have extended the applications of PGAA to additional classes of samples, especially to shale oil and oil shale samples, a variety of biological samples and high purity samples. Perhaps the most spectacular applications have been to volcanic samples from Mt. Erebus and, recently, to Mt. St. Helens. Among other things, these studies have aided in the discovery of some previously unidentified minerals.

Progress during the past year was somewhat hindered by two problems. In Sept. 1979, the NBS reactor had to be shut down until March, 1980 because of problems with shim rods that required considerable work inside the reactor itself. Secondly, just while we were in the middle of major improvements to our data-handling and -treatment system, the supplier, Tennecomp, Inc., went bankrupt. This left the system in an incomplete state. It took considerable time for us to get the partially upgraded system back into a usable condition,

1079160

but Tennecomp was not able to provide all of the planned improvements before going out of business. Because of these problems, we were not able to finish all of the projects we had planned to complete by this time. Therefore, during the remainder of the present year and during the next budget year, we plan to complete those projects, including: installation of cryogenics and single crystals in the beam, addition of a second, "singles" Ge(Li) detector on the beam line, and completion of analyses of a number of geological, energy-related samples, and high-purity samples. New projects include the extension of PGAA to more petroleum-related samples and a wider range of biological samples and follow-up studies in collaboration with the Sandia Corp. on sandstones related to bore-hole explorations for uranium.

The PGAA technique has enormous potential as a real-time, on-line method for determining the compositions of process streams in fossil fuel plants, metals industries and other kinds of plants. Because of the very long ranges of neutrons and high energy γ rays in materials, PGAA is perhaps the only method by which one can determine the bulk compositions of large, inhomogeneous samples as encountered in those applications. However, in order to make these applications possible, it will be necessary to develop portable irradiation facilities, probably based on the use of ^{252}Cf or other isotopic neutron sources. Although a considerable amount of work has been done with the use of isotopic sources, we feel that the designs of them have not been optimized in terms of the ability to observe the maximum number of elements and plan to begin some calculations and experiments leading towards such systems. One particular element that would be of very high importance to measure in these applications is oxygen. At present, the only method that is well understood requires the use of a 14-MeV neutron generator. We plan to explore other possible methods that might possibly be done with isotopic neutron sources.

1079161

II. EXTENSIONS TO NEW TYPES OF SAMPLES

A. Energy-Related Samples

Results obtained so far (1, 3 and 1980 Progress Report) indicate that PGAA can effectively measure concentrations of many major and trace elements in such energy-related samples as coal, fly ash, fuel oil, shale oil and oil shale. Studies on coal and fly ash are essentially completed now and we expect to finish those on fuel oil, shale oil and oil shale by the end of the present budget year. During the following year we plan to explore the applications of PGAA to additional petroleum-related samples including crude oil, tars, kerosene and gasoline, the latter two to demonstrate the applicability of PGAA to samples that are too volatile and hazardous for conventional analyses.

B. Geological Samples

In his thesis work, M. P. Failey (4) demonstrated the applicability of PGAA to geological samples by analyzing a large suite of USGS standard rocks, manganese nodules, etc. Some of these samples received only one irradiation. Thus, during the remainder of the present budget year, we plan to do replicate analyses of the samples as needed to finish and publish the work.

As noted in the 1980 Progress Report, PGAA has been extremely valuable in the analysis of volcanic samples from Mt. Erebus and Mt. St. Helens, including the discovery of some new, highly soluble minerals that were previously undiscovered because they are very fragile in the environment and have a physical appearance much like that of sulfur deposits. Additional samples from Mt. St. Helens continue to arrive and some of the more unusual ones will be subjected to PGAA.

1079162

C. Biological Samples

1. Human Samples

Studies now in progress on the application of PGAA to human samples are described in the 1980 Progress Report. We plan to continue our studies of various human tissues and organs. Arrangements have been made with Dr. S. H. Harrision of the National Bureau of Standards to obtain various samples from the Office of Standard Reference Material (SRM) and the National Organ Bank. Data from PGAA will be used in part to establish a new Human Liver SRM. By Sept. 1980 we will begin an in-depth study of human kidney, liver, bone marrow and brain tissue samples provided by Dr. Robert Henkin of Georgetown University Medical Center. As described in Sect. V of the 1980 Progress Report, Dr. Henkin is a coinvestigator on a project soon to be funded by USDA on the development of stable-isotope tracers in human subjects.

2. Plant and Animal Tissue

As previously described (1), we have analyzed NBS Bovine Liver (SRM 1577) and Orchard Leaves (SRM 1571) standards. In our initial studies of these materials, we were able to analyze for several important elements, including H, C, N, B and Cd, but fewer elements than in the case of crustal samples such as coal, fly ash and rocks. This result is not surprising in view of the fact that biological samples have generally lower concentrations of most elements for which PGAA is a sensitive technique. In addition, concentrations of K and Cl are greater in plant material and Cl, especially, causes considerable of interference with observations of other elements. Since these samples have not been thoroughly investigated with the use of Compton suppression and pair spectra, it may be possible to observe additional elements with the use of these techniques plus other improvements of the system described in Sect. IV.

1079163

In addition to reinvestigating the Bovine Liver and Orchard Leaves standards, we will look at a few other types of samples of botanical material. In doing so we are looking towards possible applications of portable systems in the field (see Sect. III) that would measure concentrations of elements of nutritional importance in food crops, especially N and C/N ratio (a measure of protein contents), Fe, Ca, B, etc.

We also want to explore applications to animal tissue, e.g., the Oyster standard, which we looked at briefly two years ago and newer materials under consideration for standards. In addition, we want to analyze some samples of Dissostichus mawsoni, a very unusual, deep water fish which is of considerable biological interest because of its ability to live for very long periods of time, up to 100 years and survive in the deep, cold waters around Antarctica. (See 1980 Progress Report.)

D. Intercalibration of Neutron Absorption in Sandstones

As described in the 1980 Progress Report, we have collaborated with Dr. Joseph Harris of the Sandia Corporation in a study of the composition of sandstone. The point of these studies is that of determining whether or not one can calculate the neutron-absorption properties of crustal materials simply by knowing concentrations of the elements that can be observed in those samples by PGAA and cross sections of the individual elements. If so, this would be a much more convenient, easy method than to make neutron-absorption measurements on samples of the material, as samples obtained from bore-hole cores are usually not usually not large enough for bulk neutron-absorption measurements. We plan to continue this collaborative study. If successful, this study would be of considerable benefit for field applications of PGAA by other groups as well as in our own planned studies with portable neutron sources (see Sect. III).

1079164

E. High Purity Samples

Studies on a set of boron-doped silicon samples have been completed and are discussed in the 1980 Progress Report. During the coming year, we would like to study other types of new materials in which the properties depend critically upon concentrations of elements that can be determined by PGAA, e.g., solar cell materials, glasses for light pipes. We are establishing several contacts with people in the materials fields and hope to initiate additional studies of this type.

1079165

III. FUNDAMENTAL NEW APPROACHES

A. Fundamentals of Portable Neutron-Irradiation Facilities

Although it is clear that PGAA systems based on neutron beams from reactors are going to be extremely valuable analytical tools. the applications are very much constrained by the necessity of bringing samples to a reactor. Some of the potentially most important applications, e.g., monitoring the composition of process streams in power plants or industries, can be done only with a system based on a portable source of neutrons such as a ^{252}Cf source. Many investigators have, indeed, tested the use of ^{252}Cf, Pu-Be or other isotopic neutron sources in PGAA applications (5). One of the most extensive tests has been done by a group at Science Applications, Inc. (6): they developed a system employing ^{252}Cf for irradiation of coal on a conveyor belt in which they can measure concentrations of about ten elements.

Despite the extensive amount of work done by several groups on the use of isotopic sources, we feel that there is considerable need for fundamental improvements of the method. The major limitation has been that, in order to maximize the flux of neutrons irradiating the sample, most investigators place the neutron source as close as possible to the sample consistent with other limitations such as shielding of personnel. Most neutrons emitted from the sources have high energies, the most probable energy being about 1 MeV in the case of the ^{252}Cf fission-neutron spectrum. When the source is placed close to the sample, most of the thermalization of the neutrons occurs in the sample itself, which is usually a material containing a considerable amount of hydrogen (e.g., water, coal, plastic), which is the most effective moderator (in terms of the maximum energy loss per collision).

Although the above approach may be quite adequate in many applications, we feel that there might be advantages of a system in which the neutrons were

thermalized fairly well before allowing them to enter the sample. As described in a review paper at the University of Missouri Conference in April, 1980 (7), the neutron-capture spectrum of coal fly ash obtained with our well-thermalized beam at the NBS reactor (1) contains lines for a number of elements that are not present in spectra of coal obtained by the SAI group with a ^{252}Cf source (6). The elements whose lines are missing from their spectra are those such as Sm and Gd, which have enormous cross sections. It is difficult to calculate the energy spectra of neutrons after passage through various amounts of material, but we suspect that low energy neutrons are being captured by hydrogen or other major elements that have rather flat (n,γ) absorption cross sections vs. energy before slowing down enough to be captured strongly by elements such as Sm and Gd. If this is the case, one might be able to observe more elements with a source that is surrounded by moderator that does not capture neutrons strongly, e.g., heavy water, deuterated plastic, or Be.

During the new budget year, we plan to do some calculations and preliminary tests on the design of a system in which ^{252}Cf sources would be surrounded with a moderator, reflector and shield. A major problem is that, as one surrounds the source with more material, the distance R from the source to sample necessarily increases, thus decreasing the flux at the sample approximately as $1/R^2$. In many applications, (e.g., coal on a converyor belt), the sample size could be quite large to partially compensate for the smaller flux, but the effective sample volume would be so large that the geometrical efficiency of the γ-ray detector will be reduced. Thus, some rather sophisticated calculations will be needed to design an optimal configuration of source, moderator, reflector, shielding and detection system. For the neutron energy spectrum, it will be necessary to obtain one of the

1079167

computer programs developed in the DOE laboratories to do the calculating or to obtain collaboration of a DOE group that would run them for us (e.g., the Engineering Physics Division at Oak Ridge). We will test results of some of the calculations by placing appropriate moderators around the ^{252}Cf source at the University or, if necessary, one of the stronger sources at NBS. We will test the flux in various energy regions by activation of several elements that have different types of cross-section dependences on energy. Further information could be obtained in irradiations with and without Cd absorbers around the samples.

Note that it would not be our intention to develop a complete ^{252}Cf irradiation facility this year, but rather to perform calculations and tests to determine the design of such a system to be built in the following year.

B. Oxygen Determinations with Low-Energy Neutrons

One particular element for which on-line, real-time measurements on process streams of various industries would be of considerable value is oxygen. A fairly routine method for oxygen determinations is the observation of 7-sec ^{16}N produced by the $^{16}O(n,p)^{16}N$ reaction. However, the reaction requires neutrons of higher energy than those available in quantity from isotopic sources. (There would presumably be a few neutrons in the high energy tail of the ^{252}Cf fission-neutron spectrum capable of initiating the reaction, but the activitiy of ^{16}N produced would be too small to be observed.) The reaction is normally induced by 14-MeV neutrons from a generator that employs the $T(d,n)^{4}He$ reaction. Although this is a sensitive technique for oxygen determinations, it has the disadvantage that it requires installation and considerable maintenance of the neutron generator, which includes are accelerator that produces a beam of deuterons of several hundred keV energy. It would be highly desirable to have a method available that

1079168

could use a passive, isotopic neutron source in the hostile environmental of large industrial or fossil-fuel plants.

We plan to investigate several ideas for possible determination of oxygen with isotopic neutron sources. One involves the use of the $^{18}O(n,\gamma)^{19}O$ reaction that yields 27-sec ^{19}O. The cross section is quite small (1.6×10^{-4} b) (8), but the large amounts of oxygen usually present and the high specific activity of the short-lived species may make it feasible to determine oxygen in this way. In the course of doing some very short irradiations to observe 17-sec ^{77m}Se, we observed the ^{19}O in about the amounts expected, as did previous researchers looking at the Se activity (9). However, before we can be sure if the activity is from $^{18}O(n,\gamma)$, we must check possible reactions of other elements such as $^{19}F(n,p)$. If this method is successful as performed with reactors, it would have two important implications. First, as noted in the 1980 Progress Report, when we express the concentrations of eight major elements in terms of their common oxides (e.g., Na_2O, CaO, Fe_2O_3, etc.), we find that for most crustal samples, their sum usually falls within 95 to 100% of the sample mass. Although this is a standard geochemical practice, we feel it is dangerous to estimate the oxygen concentration in this way. It would surely be incorrect, for example, if applied to some unusual volcanic samples investigated by PGAA, which contain large amounts of halogens. It would definitely be preferable to have a direct, instrumental method for actually measuring the oxygen concentration. If this method is successful, we would first use it to check the oxygen concentrations in the geological, especially the volcanic samples studied by PGAA. Second, we will consider the possibility that the method could become practical with neutrons from isotopic sources. Since the cross section is so small, it may not be practical. On the other hand, one should realize that, as we are looking at a radioactive

1079169

species with a 27-sec half life, one could observe it between beam bursts, e.g., by use of a neutron-beam chopper or, in the case of a process stream, by counting downstream from the irradiation site. These measures would eliminate prompt backgrounds associated with the neutron irradiations.

As noted, isotopic sources produce neutrons of energies too low to make ^{16}N via $^{16}O(n,p)$. However, when bombarding water with neutrons from a Pu-Be source, we observed some lines of ^{16}O that are emitted in decay of ^{16}N. Since we cannot have made ^{16}N, we think the lines may have been produced by inelastic scattering on ^{16}O, which would produce some of the same γ rays. If so, this could perhaps be developed as a method for oxygen, but would need much more investigation. If the reaction was indeed on oxygen, was it on oxygen right in the Pu-Be source itself or external to it?

During the coming year, we plan to investigate these and perhaps other methods for determining oxygen without the use of 14-MeV neutron generators.

C. X-Ray Fluorescence

The intense low energy γ-ray flux associated with the neutron beam is an undesirable interference in the capture γ-ray spectra and the installation of the Bi and/or quartz crystals in the beam (see Sect. IV.A.) is designed to reduce the interference. Despite the undesirabilty of the low energy radiation in a conventional sense, it could possibly be turned to advantage. The low energy radiations striking the target cause inner electrons to be knocked out of atoms in the target, usually followed by emissions of x rays. This is, of course, the basis of analysis by x-ray fluorescence (XRF). Although our experiments were not designed for that purpose, we have occasionally observed x-ray fluorescence lines from samples. As this might be a way of obtaining data on additional elements, we feel it would be worthwhile to investigate it further. Since the γ-ray flux is spread over many energies

rather than being a single line, as is normally used in γ-ray-induced XRF, it is not clear that this will be a useful technique. On the other hand, the γ-ray flux in our beam contains much higher energy photons than are normally used in XRF, so we should be able to excite K x rays all the way up to uranium, whereas conventional XRF has to use L lines of high-Z elements. The radiation in our system is, thus, somewhat like synchrotron radiation, but not polarized and of much lower intensities. Before we insert the crystals into the beam, we will make brief tests to see if one could obtain useful information from x-ray lines that might be observable from various elements. We will place standards of a few high- and low-Z elements in the beam and try to observe x rays with our small, high-resolution Ge(Li) detector (a Ge low-energy photon spectrometer, or "Ge-LEPS"), which yields peaks with full-width at half maximum of about 0.4 keV in the x-ray region. Runs will be made with and without a Cd foil in the beam right at floor level to see if XRF can be observed much more easily with neutrons removed from the beam. If the results indicate that this a useful method for observing some elements that we do not now observe more easily by PGAA, we will proceed to characterize the method quantitatively.

1079171

IV. SYSTEM IMPROVEMENTS

A. In-Beam Single Crystals

As indicated in last year's proposal, we are modifying the PGAA beam facility to permit installation of single crystals of bismuth and/or quartz in the beam at about the point at which the beam emerges from the top of the shielding at the NBS reactor. As described in that proposal, thermal neutrons are transmitted rather efficiently through channels of single crystals, but fast neutrons and γ rays are strongly attenuated (10). Although the thermal neutron flux in the beam will be reduced by about 50%, the fast neutrons and γ rays will be much more strongly attenuated, yielding improved detection limits for a number of elements. Scattering of the enormous flux of low energy γ rays by the samples in the beam causes such large backgrounds that it is impossible to observe any but the most intense γ rays below about 300 keV in the capture γ ray spectra of complex samples. We anticipate that several elements (especially in the rare earth region) that emit intense low energy line will become observable when the background is greatly reduced.

Another kind of background is produced by scattering of fast neutrons from the sample beam tube, etc. These scattered neutrons are often eventually captured in the structural materials of the facility (e.g., Al, Fe), producing background lines of these elements. The use of a crystal should reduce this kind of background, too, by attenuating the fast neutrons before they have a chance to undergo scattering and absorption in and near the beam tube.

We have obtained a single crystal of Bi of dimensions 10 cm long by 3.5 cm diam. We have also arranged to obtain a Bi and two quartz single crystals and their associated equipment from a neutron beam line at the Lawrence Livermore Laboratory reactor, which was recently shut down. (LLL is ready to ship the equipment as soon as we receive transfer authorization from the Oak

1079172

Ridge Operations Office.) The quartz crystal will be quite effective for attenuation of fast neutrons, but less effective than Bi for γ rays.

For highest transmission of thermal neutrons through the crystals, it is necessary to cool them far below room temperature. Thus, the crystals will be surrounded by a cryogenic system containing liquid nitrogen. We are designing a system for use of Bi or quartz crystals alone or in tandem.

When last year's proposal was written, we expected to have the crystals and cryogenics installed by this time. Although the installation may well be completed by the end of the budget year (October 31, 1980), we have been delayed because of the extended shut-down of the NBS reactor. We did not, of course, need the reactor operating to install the system, but the reactor design and construction people needed to help on this project were unavailable while the problems of the reactor were being fixed.

As soon as the system is installed, we will conduct PGAA studies on several representative types of samples (coal, fly ash, orchard leaves) to determine additional elements that become observable and find out if the accuracy and detection limits are improved for elements we now observe.

B. Addition of a Singles Detector

The upper beam tube has been modified by the addition of a second sample holder position 20 cm below the original sample position. The new sample holder will be used in connection with a "singles" Ge(Li) detector, i.e. a simple Ge(Li) detector without a NaI crystal around it, as our present detector has. Without the surrounding NaI crystal, the new detector can be mounted much closer to the samples (about 10 cm vs. 60 cm for the present detector). As demonstrated in last year's Progress Report, the NaI crystal is quite useful in the detailed study of spectra of complex samples, as it allows us to take Compton-suppressed and pair spectra as well as singles spectra.

However, once the spectra are well understood, there are many applications for which it is more important to obtain higher count rates than to obtain the other types of spectra. This, the singles detector should increase the sensitivity of the method by factors of five to ten for most elements.

After characterizing the new sample/detector set up, we will try running two samples simultaneously in the two holders. The shielding will prevent direct radiations from each sample from reaching the wrong detector. However, we may find that it is necessary to keep the first target in the beam quite thin in order to prevent neutron scattering so great that a lot of neutrons strike the second target holder and then scatter into the second detector. If this "cross talk" between the two systems is not too serious, we hope to be able to use the two systems simultaneously on a routine basis.

1079174

V. REFERENCES

1. M. P. Failey, D. L. Anderson, W. H. Zoller, G. E. Gordon and R. M. Lindstrom, Anal. Chem. 51, 2209 (1979).
2. M. S. Germani, I. Gokmen, A. C. Sigleo, G. S. Kowalczyk, I. Olmez, A. Small, D. L. Anderson, M. P. Failey, M. C. Gulovali, C. E. Choquette, E. A. Lepel, G. E. Gordon and W. H. Zoller, Anal. Chem. 52 , 240 (1980).
3. D. L. Anderson, M. P. Failey, G. E. Gordon and W. H. Zoller, Instrumental Prompt Gamma Activation Analysis of Energy Related Samples and Standards, in Proc. of the 4th Int. Conf. on Nuclear Methods in Environmental and Energy Research, Univ. of Mo., Columbia, Apr. 1980, J. Vogt, ed. (in press).
4. M. P. Failey, "Neutron-Capture Prompt Gamma-Ray Activation Analysis: A Versatile Nondestructive Technique for Multi-Element Analysis of Complex Matrices", Ph.D. Thesis, Dept. of Chemistry, Univ. of Maryland, 1979.
5. E. S. Gladney, A. Literature Survey of Chemical Analysis by Thermal Neutron Induced Capture Gamma-Ray Spectroscopy, Los Alamos Scientific Laboratory Report LA-8028-MS, Sept. 1979.
6. G. Reynolds, H. Bozorgmanesh, E. Elias, T. Gozami, T. Maung and V. Orphan, Nuclear Assay of Coal. Vol 1: Coal Composition by Prompt Neutron Activation Analysis - Basic Experiments, Electric Power Research Institute Report FP-989, Jan. 1979.
7. G. E. Gordon, The Use of Neutron-Capture Prompt Gamma-Ray Activation Analysis in Environmental and Energy Research, in Proc. of the 4th Int. Conf. on Nuclear Methods in Environmental and Energy Research, Univ. of Mo., Columbia, Apr. 1980, J. Vogt, ed. (in press).

1079175

8. C. M. Lederer and V. S. Shirley, Editors, Table of Isotopes (Wiley-Interscience, New York, 1978) 7th edit.

9. D. M. McKown and J. S. Morris, J. Radioanal. Chem. 43, 411 (1978); A. J. Blotchy, L. J. Arsenault and E. P. Rock, Anal. Chem. 45, 1056 (1973).

10. H. Zwittlinger, J. Radioanal. Chem. 14, 147 (1973); B. M. Rustad, J. Als-Nielsen, A. Bahnsen, C. J. Christenson and A. Nielson, Rev. Sci. Instrum. 36, 48 (1965).

1079176

RENEWAL PROPOSAL

TO

THE DIVISION OF BASIC ENERGY SCIENCES
U. S. DEPARTMENT OF ENERGY

"NON-DESTRUCTIVE DETERMINATION OF TRACE ELEMENT CONCENTRATIONS"

SUBMITTED BY

Glen E. Gordon, Professor of Chemistry, [redacted] Phone 301-454-4422

William H. Zoller, Professor of Chemistry, [redacted] Phone 301-454-4421

William B. Walters, Professor of Chemistry, [redacted] Phone 301-454-4421

David L. Anderson, Research Associate, [redacted] Phone 301-454-4421

Department of Chemistry
University of Maryland
College Park, Maryland 20742

Funds requested: $108,300

Contract period: November 1, 1981 - November 30, 1982

ent Contract No.: DE-AS05-76ER05173

NOTICE FOR
HANDLING PROPOSALS

"This proposal is to be used only for DOE evaluation purposes and this notice shall be affixed to any reproduction or abstract thereof. All Government and non-Government personnel handling this proposal shall exercise extreme care to insure that the information contained herein is not duplicated, used, or disclosed in whole or in part for any purpose other than to evaluate the proposal, without the written permission of the offeror (except that if a contract is awarded on the basis of this proposal, the terms of the contract shall control disclosure and use). This notice does not limit the Government's right to use information contained in the proposal if it is obtainable from another source without restriction. This is a Government notice, and shall not by itself be construed to impose any liability upon the Government or Government personnel for any disclosure or use of data contained in this proposal."

1079177

SIGNATURE PAGE

The University of Maryland will accept and administer a grant awarded to it under the terms of this proposal.

The University of Maryland is an educational institution in the State of Maryland and retains more than 500 employees.

The bidder represents that he has not employed or retained a company or person (other than a full-time employee) to solicit or secure this grant, and agrees to furnish information thereto as requested by the Contracting Officer.

The University of Maryland certifies that the distributions of costs between the direct and indirect categories as shown in the proposal conforms to the usual accounting practices of the institution for all federally supported or sponsored research.

Glen E. Gordon
Professor
Department of Chemistry

William H. Zoller
Associate Professor
Department of Chemistry

William B. Walters
Professor
Department of Chemistry

David L. Anderson
Research Associate
Department of Chemistry

James R. McNesby
Professor and Chairman
Department of Chemistry

Larry Vanderhoef
Provost
Division of Agricultural
and Life Sciences
University of Maryland

Robert L. Gluckstern
Chancellor
College Park Campus
University of Maryland

1079178

I. INTRODUCTION

This project has had a strong influence on the direction of instrumental methods of analysis. Although occasional papers on PGAA had appeared previously, the value of the method was not fully appreciated until we and, almost simultaneously, the Los Alamos group (e.g., Ref. 1) explored the full capability of it in the analysis of a wide range of materials. Now other groups have developed PGAA facilities at reactors (Univ. of Missouri and Univ. of Michigan) or are seeking funds to do so. Despite the success achieved thus far, there are still many opportunities for further development and use of the method, especially of the use of isotopic neutron sources which would permit the method to be used away from reactors.

During the coming year we propose to continue the fundamental development of PGAA by studies of oil shale, bore-hole samples, industrial materials of various types, biological material and to do fundamental studies of prompt γ rays and the short-lived fission-product γ rays produced by heavy elements under neutron irradiation. The sensitivity of the system has been improved by addition of the second target/detector station on the beam line, which will greatly increase the throughput of samples. We have acquired several crystals for use as filters of γ rays and fast neutrons from the beam and will place one of them in the system as soon as tests on them are complete. The data-handling system, which has caused us a great deal of down-time in the wake of Tennecomp's bankruptcy, should be brought up to its intended capability when equipment on order arrives in July, 1981.

The major new venture for the new year will be work on the development of a ^{252}Cf-based PGAA system. A source of ^{252}Cf has been installed at the University. Calculations will be performed and tested experimentally in an attempt to optimize the moderator, shielding and placement of samples and the detector. A wide range of samples will be analyzed with the facility to determine its capabilities in many potential applications.

1079179

II. NBS BEAM FACILITY

A. Energy-Related Samples

1. Oil Shale

We have been involved in a collaborative effort with Dr. C. L. Wilkerson of Battelle Pacific Northwest Laboratories, with the aim of characterizing a large batch of Greer River (Colorado) oil shale for a large number of elements. This material is to be established as a standard reference material through round-robin analyses by Battelle, University of Maryland, Lawrence Berkeley and Lawrence Livermore National Laboratories (see 1981 Progress Report). Rather short irrdiations (2-hr) by PGAA were performed to characterize 16 elements in the shale, but longer irradiations are proposed to establish the concentrations of several other elements, especially C, N and, possibly, Sr and Nd.

A well-characterized standard such as this would be extremely valuable to energy research in this field. Our PGAA results for these and other energy-related samples have caused great interest among several corporations, including one major oil company, which is interested in boron measurments, a fast, routine procedure with PGAA. We have initiated discussions with scientists at the company in regard to possible cooperative projects.

The success of PGAA in the analysis of oil shale has led to the proposal for more joint work with Battelle. During the following year we propose to continue the analyses of other oil shales (raw and retorted) as well as looking into new types of samples, including shale oil itself.

2. Heavy Elements

A major problem of the nuclear energy industry is that of assaying various fissile nuclei in spent fuel rods and in process streams in fuel reprocessing plants. Much progress has been made in the assay for a number of

1079180

fissile nuclides by high resolution Ge(Li) spectrometry of heavy element x-rays and low energy γ rays by Camp and others at Livermore (2); however, this method can be used only if the heavy elements are free of other activities. It would be extremely useful to have a method for measuring the heavy elements in the presence of fission products that would normally be associated with fuel rods after a typical burn-up in a reactor followed by several months cooling. We have performed calculations that indicate that several fissile species might be measurable by PGAA methods despite the enormous γ-ray activity of fission products in spent fuels. In one approach, one would look at prompt γ rays following (n,γ) reactions of the heavy elements. Our calculations show that it might be feasible to measure ^{238}U, ^{239}Pu, ^{240}Pu and ^{241}Pu by this method. The reasons for the possible success of this method are: (1) thermal neutron cross sections for many of the heavy elements are quite large (as they must be for important fissile species), and (2) the prompt γ rays chosen for the measurements have energies >4 MeV, whereas those of the long-lived fission products are mostly <900 keV, allowing one to discriminate strongly against the latter by placing absorbers between the sample and the Ge(Li) detector.

This method would probably not work for some important species, especially ^{235}U, which does not have strong capture lines. However, a second possible method would be the observation of γ rays from very short-lived fission products (seconds or less), some of which have energies >4 MeV. To avoid confusion with prompt γ rays and other interferences associated with the beam, one would use a beam chopper and accept signals only between beam bursts of about 1-sec duration. Note that fission products would result from irradiation of all abundant fissile species, but the intensity patterns would be different for the various nuclides because of different yield-mass

1079181

distributions, especially in the A=95-105 region.

We have discussed these approaches with Safeguards and Fuel Cycle groups within DOE. Although they are interested, there are so many unknown factors involved that we cannot a priori prove the feasibility of the method. Thus, we have not been able to convince them of the probable success of the method enough for them to support the study. Therefore, during the coming year we plan to irradiate several heavy element samples in order to obtain sufficient data on capture and fission-product spectra that we can make more reliable predictions of the feasibility. These will be strictly fundamental studies designed to provide sufficient spectral data for preductions. If the predictions indicate a good chance of success, continued practical development of the method would be done only under support of another funding group. Scientists from Battelle Northwest Laboratories are also interested in obtaining these data and are providing a number of heavy element samples for the experiments. We have received permission and plan to irradiate small samples of Gd-poisoned solutions of uranium enriched in ^{235}U and two Pu samples in order to explore possibilities for PGAA in nuclear safeguards and the measurement of nuclear materials.

3. Reactor Cooling Water

Another kind of sample that is subjected to intense and frequent neutron irradiation is reactor cooling water. There is much practical concern about the radioactive species present in cooling waters, first because the information would be of great value in case of a leak and, second, because the species could be useful indicators of problems that might be occurring in the reactor. As all materials that get into the water undergo intense neutron irradiation, one could probably detect corrosion products or other materials

1079182

that get into the circulating water. We have been discussing the possibility of making some observations of the cooling water at the Calvert Cliffs power plant with people from Baltimore Gas and Electric Company. If the logistics can be worked out, we plan to take spectra of the cooling water in the plant to look for short-lived γ-emitting nuclides. If the results are interesting, we will seek other sources of support for development of a practical method. One can imagine that, if the work is successful, it might become a standard method for monitoring cooling water at reactors in order to observe potential problems in the system before they cause serious accidents.

B. Related Geochemical Samples

1. Bore-Hole Samples

We plan to continue the collaborative effort with Dr. H. Bivens and Dr. J. Harris of Sandia Laboratories involving neutron-capture cross-sections of bore-hole samples (see 1981 Progress Report). The major objective of this joint effort is the development of *in situ* measurements of the compositions of wall materials around bore-holes using a small 14-MeV neutron generator and Ge(Li) detector package that can be lowered into the bore holes.

2. Ores

One of the potentially exciting uses of a portable PGAA system based on ^{252}Cf is that of prospecting in the field in search of resources such as ores of various metals. In order to provide fundamental information needed to determine the feasibility of such uses, we plan to take prompt γ-ray spectra of representative ores of several metals. Already we have samples of a number of copper ores from several areas in Arizona that were obtained in connection with our INAA studies of particles released to the atmosphere from Cu smelters (3). We will be contacting people from other mines and smelters as well as the U.S. Geological Survey and the Bureau of Mines to obtain samples of other types of ores for these experiments.

1079183

3. U.S. Geological Survey Standard Rocks

In his thesis work (4), Michael Failey explored the use of PGAA by measuring concentrations of all observable elements in a wide range of USGS standard rocks. For the most part, the results were excellent and we would like to publish them. We have not done so, however, because he performed only one analysis of several of the rock types. As soon as time is available on the system, we plan to irradiate additional samples of those needed in order to finish and write up the project.

C. Biological Samples

1. General Studies of Feasibility

There is considerable interest in the development of analytical methods for biological materials, especially tissues in or from human bodies. Several groups, for example, are working on *in vivo* measurements of Cd in liver and kidneys (5) in workers exposed to large amounts of Cd, of Ca in patients suffering from bone diseases (6), and of N to determine proteins in the body (7). Some of these studies are performed by observing prompt γ rays (Cd) and others by production of short-lived activities (N and Ca). To provide better methods for these and *in vitro* studies, we have been analyzing various organs and tissues of human bodies obtained from autopsies performed at Georgetown University Medical Center to determine which elements are observable by PGAA and measure their concentrations in those samples. We plan to obtain additional samples to extend this work. Related to this work, we are setting up an arrangement to analyze liver samples which are being collected in large numbers by the National Specimen Bank at NBS. They plan to provide funds for support of a person who will do the PGAA measurements as well as some regular INAA and for supplies and reactor charges connected with their work. The Specimen Bank will also be analyzing and storing mussles collected from the

1079184

various coastal waters of the U.S., the idea being that these are "indicator" organisms, i.e., filter feeders that are constantly collecting and storing chemicals present in the water and, thus, will provide an historical record of changes that may be caused by natural or anthropogenic effects. Some of the mussles will also be analyzed by PGAA and other methods under our joint project with NBS.

2. Stable Isotopic Tracing

In a joint project with Georgetown University Medical Center that is supported by the U.S. Department of Agriculture, we (GEG and NKA) are developing the use of stable isotope tracers for studying trace element nutrition in population groups that are prohibited from study with *in vivo* radioactive tracers. The basic idea is that one administers a dose of the element in which the abundance of a minor stable isotope has been greatly enriched relative to its natural abundance (e.g., ^{70}Zn for tracing Zn). The appearance of the tracer in various body "pools" (e.g., blood, serum, feces, urine) is detected as an altered ratio of isotopes, e.g., the $^{70}Zn/^{68}Zn$ ratio. We have been developing nuclear activation methods for determining changes in the isotope ratios, e.g., in the Zn case, measuring the ratio of 3.9-hr ^{71m}Zn to 14-hr ^{69m}Zn following neutron activation.

PGAA might also be useful for determining ratios of isotopes, as the spectra of many element that have more than one stable isotope contain lines from capture in various isotopes. In order to avoid contamination of the samples, we have tried to observe as many isotopes as possible by instrumental methods. As described in the Progress Report, we studied blood samples by PGAA, but because of the intensity of Cl lines in the spectra, we could observe only H, C, N, S, Cl and K, none of which is a good candidate for stable isotope tracing. However, there still might be a role for PGAA if one chemically separates the element of interest prior to PGAA. In the absence of

1079185

interference by other elements, it might be possible to observe lines of more than one isotope, or measure one isotope by PGAA and another by INAA. We will soon be starting experiments with enriched-isotope samples of Zn and Se in our USDA project. At that time, we will do PGAA on enriched-isotope and natural samples of those elements to see if there are differences that could exploited in that work.

If stable isotope tracing can be successfully developed for in vivo human studies, it might well have many other applications in areas where radioactive tracing is used, but is undesirable because of exposure to people or sensitive materials, e.g., semiconductor materials.

D. Industrial Samples

From the outset of this project, we have felt that there would eventually be many industrial applcations of PGAA, especially if portable systems based on ^{252}Cf or other isotopic sources could be developed. The method has many obvious applications for real-time analysis of large, inhomogeneous materials. Because of the long ranges of the neutrons as well as the γ rays, PGAA can measure bulk concentrations in those materials, whereas other real-time instrumental methods such a x-ray fluorescence are only surface methods because of the short-range radiations involved. Thus, PGAA should be very useful for monitoring streams of raw materials or products in large industrial plants. A group at Science Applications, Inc. (8), for example, has demonstrated the ability of a ^{252}Cf-based PGAA system to analyze coal on a conveyer belt for about ten elements including S as well as several elements that indicate the ash content of the coal. Their system is now undergoing pilot-plant studies in an actual coal-fired plant.

Thoughout this project, we have made many efforts to be in touch with scientists in many industries in order to learn about their analytical needs

1079186

and to inform them of the potential for using PGAA. We have hoped to encourage them to provide funds for development of techniques needed specifically by them. Although we have obtained some very minor support for collaborative work with Sandia Corp. (see Sect. II.B.1.) on development of bore-hole analyses and will probably receive modest support from the National Specimen Bank for collaborative studies of biological samples (see Sect. II.C.1), we have not been able to interest industries in providing major support. Many groups have expressed great interest in our work, but are apparently not persuaded on the basis of our past work coupled with feasibility calculations involving their particular problem. Thus, we feel that it will be necessary to demonstrate analyses of typical industrial materials and are planning to do some of these over the next year. Among others, we have established contacts with scientists at a steel mill, several copper smelters, an oil company, a photographic company, a glass manufacturer, two major automobile companies, and a communications-industry laboratory. In part as a result of these contacts, we will extend our studies of oil shales (Sect. II.A.1) and bore-hole samples (Sect. II.B.1.) and initiate studies of ores (Sect. II.B.2), glasses, steel, limestone and special materials of the communications industry, as discussed below.

1. Glasses

From contacts with a glass manufacturer and with the automotive glass division of a motor vehicle company, we have found that, despite the sophistication of modern glasses (e.g., those designed for energy conservation in buildings), the glasses are made in batch processes under rather poor analytical control. The latter is so inadequate that some batches turn out so badly that the entire batch is remelted so that the composition can be corrected. The PGAA method should be an ideal method for real-time

1079187

measurements in the industry, as it is sensitive to most of the key elements present in glass. In addition to the major elements, glass manufacturers add large amounts of what are normally considered trace elements for special purpose glasses (e.g., Se and Cd in tinted glasses). If these elements cannot be measured directly by PGAA, it may be possible by activation, in this example, of 17-sec ^{77m}Se with the ^{252}Cf source, as we are able to observe it following short irradiations of blood in the NBS reactor (9). We have already acquired a wide range of glass samples for analysis.

2. Steel and Limestone

There are many process streams in the steel industry that would be of interest for real-time analysis, including the incoming ore, limestone, coke and the finished products. Steel industry scientists visited us and were quite interested in the possible use of PGAA. They are interested in measuring several elements that we can surely do, inlcuding Fe, Si and Ca, but are especially interested in oxygen measurements, if they can be done without the use of a 14-MeV neutron generator. From our previous work, we are confident that O can be measured in many types of samples by very short irradiations in the reactor followed by observation of 26-sec ^{19}O. However, it will be of much greater value if we can observe it with the ^{252}Cf source. Calculations suggest that it is going to be difficult, but worth trying. We will investigate this as well as the possibilities for the $^{16}O(n,n'\gamma)$ reaction with the high energy neutrons from the ^{252}Cf source as soon as possible. We will also obtain samples of ores, limestone, steel, etc. from the company for survey experiments in the NBS beam line.

3. Communications Industry

We don't yet know a great deal about the analytical problems of the communications industry, but made contact with scientists from the industry at

1079188

the recent Modern Trends conference in Toronto. We discussed the method and what it can do and have sent the reprints. They were especially interested in our boron measurements in Si or glassy matrices, so we will try to learn more about their problems and perhaps run a survey on some samples from them.

E. Facility Improvements

1. Beam Filters

The Bi single crystal obtained has been evaluated for neutron transmission with the help of R. Fleming of NBS (see 1981 Progress Report). Installation in the PGAA facility has been delayed by unforeseen problems in the construction of a suitable cryostat assembly for the existing beam tube. It is likely that a new section will have to be constructed and attached to the beam tube which can properly cool the Bi and still have enough shielding to protect our detection system.

Alternative filter systems are being considered, including an Si crystal and a sapphire crystal. Preliminary studies, also by R. Fleming, have been completed and indicate that the latter may be a desirable alternative, since no cooling is necessary. If a non-cooled crystal could be inserted into our beam shutter, very few scattering problems are anticipated.

2. Second Target/Detector Station

The second target/detector station has been installed and our initial tests indicate that the sensitivity in that position is about an order-of-magnitude better than for our original set-up (see 1981 Progress Report). However, before putting the new station into routine use, we must make several additional tests. Mainly we need to find out if both stations can be used simultaneously, or if scattering of neutrons by targets placed in the new station (which is "upstream") will increase backgrounds or otherwise interfere with simultaneous measurements at the original position.

1079189

3. Beam Chopper

We propose to do preliminary studies on "chopping" the neutron beam in order to study short-lived neutron activation species and fission products. A simple way to investigate this could be to simultaneously control a simple, lightweight Cd shutter at floor level, while gating the corresponding ADC off when the beam is on target. Our group has experience with such systems at the Maryland Cyclotron (10). The chopper, coupled with the better sensitivity of the second detector could open up a new set of elements for analysis.

1079190

III. CALIFORNIUM-252 FACILITY

As proposed last year and described in the Progress Report, we have acquired a 150-μg ^{252}Cf source for development of PGAA applications that can be done away from the reactors. Although we initiated paperwork to obtain approval to acquire the source in Nov. 1980, the long delays in processing the forms kept us from getting it until late May, 1981. Thus, we have not had time for much work on it, but will be doing so over the remaining months of this budget year and into the new year. There are 4 additional 150-μg sources at NBS and we may be able to obtain 3 of them to bring the total up to 0.6 mg, which would greatly improve the sensitivity of measurements.

A. Configuration Tests

There are many parameters involved in the design and construction of isotopic neutron sources and associated target holders and detectors, e.g., the choice of materials and sizes of moderators, the size and placement of samples, and material for reflecting and absorbing neutrons, γ-ray and neutron shielding of detectors and personnel, and location of the detector. Although a number of designs are given in the literature, it is not obvious that any of them provide optimal sensitivity with minimum interference for quantitative work. Calculations of the flux and energy spectrum of neutrons at various locations within a particular configuration are very complicated and can be done accurately only with the use of large computer codes developed by AEC and its contractors for use in reactor and weapon design. Examples of some calculations performed by SAI for design of their PGAA system are available (11), but they are based on a very simple model. Fortunately, as a part of our arrangement with the Sandia Corp., they will run a number of calculations for us of several configurations using their very complex codes. Soon we will send them the suggested arrangements and when the calculations have been

1079191

completed, we will perform tests of the most promising configurations by placing samples of Au, Dy, etc., at various locations, with and without Cd envelopes, to measure fluxes and Cd ratios. These results will be used to design and construct the final ^{252}Cf facility.

B. Analytical Tests

As soon as preliminary experiments have been completed, we will test the analytical capabilities of the ^{252}Cf facilities. In the initial studies, most measurements will be done on standard materials that we have previously analyzed in detail at the NBS facility to see if the results obtained with ^{252}Cf are reliable or if there are differences caused by the presence of higher energy neutrons in the latter source. Once the system has been tested by analysis of standards, we will then use it for survey studies of a wide range of materials mentioned throughout this proposal, especially in Sect. II. Most materials will first be run on the NBS beam line, which will produce higher count rates for most species. Whereas we normally use about 1-g samples in the beam facility, we will often use much larger samples (e.g., 1 kg) in the ^{252}Cf facility, if large amounts of material are available. This will increase count rates of the γ rays and also provide a better simulation of the bulk samples that would be encountered in field and industrial applications. A study of specific interest on the ^{252}Cf facility will be a search for lines associated with oxygen, either prompt lines from $(n,n'\gamma)$ or delayed emissions from 26-sec ^{19}O. In order to observe radiations from very short-lived species free of the backgrounds present in the target area, provision will be made in the facility for a flowing system with a detector mounted downstream from the irradiation site.

C. Detector for ^{252}Cf Facility

One of the difficulties associated with the use of ^{252}Cf neutrons for

1079192

quantitative analytical measurements is exposure of the γ-ray detector to fast neutrons. We have used an older Ge(Li) detector initially damaged by neutrons in in-beam experiments at the Maryland Cyclotron. Our initial tests have resulted in continued degraduation of the performance of this detector. In the budget, we propose the purchase of a new n-type hyperpure Ge detector for use in these experiments. As these n-type Ge detectors are more resistant to damage by fast neutrons (R. H. Pell, Physics Today, November, 1977), we expect to be able to carry out our tests with use of the ^{252}Cf neutron source with limited degradation of the detector performance.

1079193

IV. REFERENCES

1. E. S. Gladney, D. B. Curtis and E. T. Jurney, J. Radioanal. Chem. 96, 299 (1978).
2. G. Struble, editor, Nuclear Chemistry Division Annual Report, FY 1980, Lawrence Livermore National Laboratory Report UCAR-10062, Aug. 1980.
3. M. Small, M. S. Germani, A. M. Small, W. H. Zoller and J. L. Moyers, Environ. Sci. Technol. 15, 293 (1981); M. S. Germani, M. Small, W. H. Zoller and J. L. Moyers, ibid. 15, 299 (1981).
4. M. P. Failey, Ph.D. Thesis, Dept. of Chemistry, Univ. of Maryland, College Park, MD, 1979.
5. D. Vartsky, K. J. Ellis, N. S. Chen and S. H. Cohn, Phys. Med. Biol. 22, 1085 (1977); P. E. Cummins, J. Dutton, C. J. Evans, W. D. Morgan and A. Sivyer, "A Sensitive ^{252}Cf Neutron Activation Analysis Instrument for In-Vivo Measurements of Organ Cadmium," presented at the Sixth Int. Conf. on Modern Trends in Activation Analysis, Toronto, June, 1981.
6. J. E. Harrison, K. G. McNeill, A. J. Hitchman and B. A. Britt, Inv. Rad. 14, 27 (1979).
7. D. R. Chettle, J. G. Fletcher, S. P. M. J. Downey, M. C. Scott, H. M. James and C. S. Higgens, "Measurement of Nitrogen In Vivo by Neutron Activation Analysis; Further Developments and Applications," presented at the Sixth Int. Conf. on Modern Trends in Activation Analysis, Toronto, June, 1981.
8. G. Reynolds, H. Bozorgmanesh, E. Elias, T. Gozani, T. Maung and V. Orphan, Nuclear Assay of Coal. Vol. 1: Coal Composition by Prompt Neutron Activation Analysis - Basic Experiments, Electric Power Research Institute Report FP-989, Jan. 1979.

1079194

9. G. E. Gordon, I. Gokmen, N. K. Aras and R. I. Henkin, "The Use of Stable Isotope Tracers in the Study of Zinc and Selenium Nutrition in Infants," presented at the Sixth Int. Conf. on Modern Trends in Activation Analysis, Toronto, June, 1981.

10. E. W. Schneider, Ph.D. Thesis, Dept. of Chemistry, Univ. of Maryland, College Park, MD, 1978.

11. E. Elias and T. Gozani, Nuclear Assay of Coal. Vol. 2: Coal Composition Determination by Prompt Neutron Activation Analysis - Theoretical Modeling, Electric Power Research Institute Report CS-989, Apr. 1980.

1079195

V. BUDGET

University of Maryland

Contract DE-AS05-76ER-05173

November 1, 1981 through November 30, 1982

A-II(a) - REIMBURSABLE OR COST-SHARING PORTION

1. Salaries and Wages

Scientific Discipline Personnel

Principal Investigator, G. E. Gordon, Professor 20% summer 1982	$ 2,200
Principal Investigator, W. H. Zoller, Professor 25% summer 1982	$ 2,250
D. Anderson, Research Associate - 100% of time for 13 months	$ 24,000
2 Graduate Assistants C. M. Thompson, 100% of time for 13 months S. Bradley, 100% of time for 2 months summer	 $ 8,000 1,350
SUB TOTAL	$ 37,800

2. Indirect Costs 41% x 60,000 MTDC on items 1, 3, 5, 6, 7a and 7b	$ 24,600
3. Supplies and Materials	$ 5,000
4. Equipment n-type hyperpure Ge detector electronic modules	 $ 13,000 1,200
5. Publications	$ 2,000
6. Travel - Domestic ACS Meetings Las Vegas and Kansas City Trips to NBS reactor from University of Maryland campus	$ 4,000
7. Other	
a. Fringe Benefits Hospitalization @ $115/month married, 19.48 single 20% faculty rate (Walters 7.3%) 7.3% Gordon and Zoller	$ 7,200
b. Maintenance	$ 4,000
c. Reactor subcontract	$ 9,500
TOTAL	$108,300

1079196

A-II(b) - ITEMS EXCLUDED FROM COST-SHARING TO BE FURNISHED BY UNIVERSITY

none

A-II(c) - UNIVERSITY CONTRIBUTION OF PRINCIPAL INVESTIGATOR

Principal Investigators

G. E. Gordon
10% of time for 9.5 months - academic year

W. H. Zoller
10% of time for 9.5 months - academic year

W. B. Walters
10% of time for 9.5 months - academic year

1079197

VI. OTHER SOURCES OF RESEARCH SUPPORT

A. Current Support

1. Zinc, Selenium and Chromium Nutrition in Term and Pre-Term Infants, Gordon (with R. Henkin, K. Sivasubramanian and R. Aamodt) USDA, $43,000, 9/15/80-9/30/81. Gordon, 10% of acad. year, 1 month summer.

2. The Composition of Remote Area Aerosols from Antarctica and Hawaii, Zoller, $58,000, NOAA, 2/1/81-1/31/82. Zoller, 10% of acad. year, 1 month summer.

3. Radioactive Decay Studies at TRISTAN II; Walters, DOE, $88,000, 7/1/80-6/30/81. Walters, 25% of acad. year, 2.5 months summer.

4. The Importance of Organic Slicks on Water Surfaces Near Power Plants on Chesapeake Bay; Zoller and Jon M. Bellama (U. of Maryland), State of Maryland, $40,688, 8/15/80-8/14/81. Zoller, 5% of acad. year.

5. Volcanic Impact on Stratospheric Aerosol Chemistry; Zoller, NASA, $60,000, 3/1/80-11/30/82. Zoller, 5% of acad. year.

6. Interpretation of the RAPS Atmospheric Elemental Concentration Data, Gordon, $62,000, EPA, 11/16/80-11/15/81. Gordon, 10% of acad. year, 1.5 months summer.

7. Cooperative Study of Bore-Hole Samples, Gordon and Zoller, Sandia Laboratories, $5000, 2/18-12/81.

8. Research on Atmospheric Volcanic Emissions, Zoller and James P. Friend (Drexel University), NASA, $156,000, 5/15/81-5/14/82; Univ. Md. portion, $65,000. Zoller 10% acad year, 1.5 months summer.

B. Pending Support

1. Zinc, Selenium and Chromium Nutrition in Term and Pre-Term Infants, Gordon (with R. I. Henkin, K. Sivasubramanian and R. Aamodt), $49,889, USDA, 9/15/81-9/14/82. Gordon, 10% of acad. year, 1 month summer.

2. Development of Receptor Models for Atmospheric Particles, Gordon, EPA, $225,076 for 3 years. Gordon 10% of acad. year, 1.5 months summer.

3. Radioactive Decay Studies at TRISTAN, Walters, DOE, $144,000 7/1/81-4/30/83. Walters 20% of acad. year, 2.5 months summer.

1079198

VII. FINANCIAL STATEMENT

1.	Total actual project cost to date for the current period	$ 570,200
2.	Estimated total cost for remainder of period	24,780
3.	Total actual and estimated cost chargeable to DOE for current period based on percentage of cost agreed upon as contained in A-III of Appendix "A" to Contract	594,981
4.	Accumulated costs chargeable to DOE (incude costs reported in certified statement for preceding period(s) and the costs stated in Item 3 above)	594,981
5.	Accumulated DOE Support Ceiling as stated in Article III of Contract	594,981
6.	Total estimated DOE funds remaining under Contract subtract Item 4 from 5 which may be used to reduce amount of new funds required from DOE for proposed period	0