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NON-DESTRUCTIVE DETERMINATION OF TRACE-ELEMENT CONCENTRATIONS

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TABLE OF CONTENTS

Section		Page
I.	INTRODUCTION	3
II.	NEW TYPES OF SAMPLES	7
	A. Energy-Related Samples	7
	B. Volcanic Samples	11
	C. Biological Samples	18
	D. Neutron-Capture Cross Section of Bore-Hole Samples	22
	E. Boron in Semiconductor Silicon	24
III.	RECOMMEND γ-RAY LINES FOR QUANTITATIVE DETERMINATIONS	27
IV.	SYSTEMS IMPROVEMENTS	34
	A. Beam Filter System	34
	B. Second Sample Position	34
	C. Data-Handling Facilities	35
V.	RELATED PROJECT SPIN-OFFS	37
VI.	PUBLICATIONS AND ADDRESSES	39
VII.	PERSONNEL	41
VIII.	REFERENCES	42

1079201

I. INTRODUCTION

During the past year, the tremendous capabilities of neutron-capture prompt γ-ray activation analysis (PGAA) became apparent to a much wider community of potential users. Prior to this year, our group and a group at Los Alamos Scientific Laboratory (Gladney, Curtis and Jurney) were the only groups in the U. S. with a major involvement in development of reactor-based PGAA methods. This year a third group, at the University of Missouri reactor (Vogt, Glascock et al.), finished construction of a system and began major experiments. From contacts with other groups and, especially, discussions at the Fourth International Conference on Nuclear Methods in Environmental and Energy Research at the University of Missouri in April, it is clear that the research community has recognized the value of the method and several additional groups are starting to build facilities for using it.

In this year's Report, we cover the extensions of PGAA to several new types of samples. The more we investigate new applications, the more we are struck by some of the attributes of PGAA, especially as applied to crustal type samples. Although PGAA is quite sensitive for several trace elements (notably B, Cd, Sm and Gd), it is an excellent technique for major elements in the Earth's crust. By using the common geochemical technique in which one expresses the masses of major elements as their common oxides (i.e., Na_2O, CaO, SiO_2, etc.) and summing the weight concentrations of the oxides (usually of the eight elements Na, K, Mg, Ca, Al, Si, Ti and Fe, which we normally observe), we typically account for 95 to 100% of the sample mass. This feature is especially demonstrated in the case of Mt. St. Helens ash and other volcanic samples (Sect. III.B). Despite this good agreement, we feel that the use of common oxides is dubious and plan to develop a method for oxygen measurements in the coming year. Although in the work we did on National

1079202

Bureau of Standards (NBS) standards (1), we usually irradiated samples for 12 to 24 hrs in order to obtain very good statistics on weak lines, in this report we show that good quality analyses can be obtained in as short as two hours (shown in several sections). Addition of a second Ge(Li) detector without a NaI crystal around it, which will occur soon (see Sect. II.B), will allow us to move the Ge(Li) detector much closer to the samples to increase counting efficiencies and further reduce the irradiation times needed to achieve a given statistical uncertainty.

Another major attribute of PGAA, which becomes important for study of a rapidly changing phenomenon such as the Mt. St. Helens volcano, is that one obtains results very quickly. Since the data are all available as soon as the irradiation is finished, one can have PGAA results completed within a few hours after receipt of a sample. If anything unusual turns up in the results, there may be time to pursue it by collection of additional samples before the phenomenon changes. This rapid turn-around time for analyses is to be contrasted with instrumental neutron activation analysis (INAA), which requires about three weeks for complete analyses, or more conventional chemical analyses, which require several days for dissolution and separations. The latter methods are, of course, still of great value, as they can be used to assay many species that cannot be observed by INAA.

The PGAA method is clearly going to be of considerable use in the analysis of energy-related samples and, in particular, fossil fuels. We have already demonstrated the applicability of PGAA to coals and fly ashes (1) and, during the past year, we began studies of oil shales, shale oil and oil (Sect. III.A.). The oil shales can be analyzed for about the same elements and for coal and fly ash, but the shale oil and other oils are much more difficult to analyze and will require further work during the coming year. We are also

1079203

beginning to analyze more biological samples (Sect. II.C.), but they, too, are going to require considerable more work as the spectra contain many strong lines from Cl and the concentrations of most elements that we observe in crustal samples are much lower in biological samples.

We have demonstrated a case of the analysis of a high purity type of sample, namely high purity silicon doped with various amounts of B (Sect. II.E.). Measurements of B were performed down to the 1 μg/g level, but could be taken down at least another order of magnitude by using larger samples and longer irradiation times. The lowest B concentration measured so far has been 0.24±0.08 μg/g in USGS rock BIR-1 (North Carolina Diabase).

Some of the most important applications of PGAA are going to be those in the field using portable neutron sources, e.g., monitoring the compositions of process streams in fossil fuel or other industries, geological prospecting, studies of planetary surfaces, etc. During the past year we initiated a small step in that direction by collaborating with Dr. Joseph Harris of Sandia Corp. on studies of sandstone related to the use of bore-hole logging data (see Sect. II.D).

One of the difficulties encountered in the development of PGAA has been the lack of detailed, reliable lists of the best γ rays to use for the analyses for various elements along with the interferences with these γ rays that can be expected. We have produced tabulations of this information based on studies of elemental and simple compound spectra taken for 31 elements that we have observed in one kind of sample or another (Sect. III). These tabulations have been published in the thesis of Dr. M. P. Failey, the first student in the group to receive a Ph.D. primarily for PGAA work.

As we anticipated, once we were able to demonstrate the applicability of PGAA to various types of problems, we began to develop interest in other

1079204

agencies for funding of projects that would use PGAA. As noted in Sect. V, we anticipate funding from the U. S. Department of Agriculture for the development of stable-isotope tracers for use in humans. Funding has also been obtained for various studies of volcanoes in part on the basis of the excellent results obtainable by PGAA.

Although much has been accomplished during the past year on this project, progress in some areas was not as rapid as we had anticipated for two reasons that were beyond our control. In Sept. 1979, the NBS reactor developed problems with the shim-rod controls inside the reactor. The problem was serious enough that it required a considerable amount of work to be done inside of the reactor. For this reason, the reactor was shut down from Sept., 1979, until March, 1980. Fortunately, the work was successful and the reactor is again running smoothly. Second, as discussed in Sect. II.C., right in the middle of an upgrading of the data-acquisition and -treatment system, the supplier, Tennecomp, went bankrupt, leaving the conversion incomplete.

1079205

II. NEW TYPES OF SAMPLES

A. Energy-Related Samples

Several types of energy-related materials were analyzed by PGAA as reported at the Missouri Conference (2). The effectiveness of the technique for the determination of up to 17 elements in coal and coal fly ash standards in long (15 to 20 hrs) irradiations was previously demonstrated (1). We have now found that for much shorter irradiation times (2 to 3 hrs), the elements B, Na, Al, S, Cl, K, Ti, Fe, Sm and Gd in power-plant coal samples can be routinely analyzed (see Table 1, last column).

A number of oil-shale and shale-oil samples were obtained from C. L. Wilkerson of Battelle Northwest Laboratories, and were analyzed by PGAA (Tables 2 and 3). For the oil shale, 2.5-hour irradiations were sufficient to provide accurate determination of 14 elements: H, B, Na, Mg, Al, Si, S, K, Ca, Ti, Fe, Cd, Sm and Gd.

Samples of two types of shale oils (both ground-level- and *in situ*-derived shale oils), as well as SRM 1634 (#6 fuel oil), and both high-sulfur and low-sulfur fuel oils obtained from Potomac Electric Power Co., were irradiated. The results are given in Tables 3 and 4. The PGAA method proved to be very reliable for the determination of V in the SRM and high-sulfur oil, while S was readily measured in all the oils tested. In addition to S, both B and N could be analyzed in the shale oil samples. Peaks from these elements are present in the spectra, but we have not yet measured the concentrations.

1079206

Table 1. Concentrations of Elements in Coals as Determined by PGAA

Element	SRM 1632		SRM 1632a		SRM 1635		Chalk Point Power Plant Coal
	PGAA[a]	Other[b]	PGAA[a]	Other[c]	PGAA[a]	Other[c]	PGAA[d]
H (%)	4.02±0.05	4.3	3.7±0.1	-	3.96±0.03	-	-
B (μg/g)	42.1±0.7	47.0	53±2	-	105±3	-	10.7±0.5
C (%)	70±5	73	71±4	-	59±3	-	-
N (%)	1.3±0.2	1.2	1.27±0.08	-	1.0±0.1	-	-
Na (%)	-	0.041	-	0.085	0.270±0.005	0.244	0.15±0.05
Al (%)	1.68±0.04	1.85, 1.74	3.01±0.13	3.07, 2.91	0.34±0.04	0.32, 0.30	1.6±0.3
Si (%)	2.95±0.06	3.2, 3.92	5.8±0.1	-	0.52±0.02	0.56	-
S (%)	1.29±0.03	1.32	1.59±0.02	1.64, 1.8	0.32±0.01	0.33	2.41±0.03
Cl (μg/g)	895±15	890	784±17	780	26±2	26	740±30
K (%)	0.275±0.010	0.28	0.42±0.02	0.42	0.0097±0.0006	0.0117	0.21±0.03
Ca (%)	0.33±0.05	0.35	0.24±0.02	0.24	0.54±0.02	0.55	-
Ti (μg/g)	890±35	800, 890	1550±40	1750, 1620	190±20	200, 205	880±30
Mn (μg/g)	43.5±2.4	40±3	29±5	28±2	24±7	21.4±1.5	-
Fe (%)	0.84±0.02	0.87±0.03	1.11±0.06	1.11±0.02	0.22±0.01	0.239±0.005	1.75±0.19
Cd (μg/g)	0.18±0.02	0.19±0.03	0.21±0.03	0.17±0.02	-	0.03±0.01	-
Nd (μg/g)	11.3±2.0	8.7	11.8±0.4	-	-	-	-
Sm (μg/g)	1.53±0.02	1.7	2.10±0.07	-	0.25±0.01	-	2.1±0.2
Gd (μg/g)	2.20±0.08	-	3.00±0.05	-	0.35±0.02	-	2.8±0.4

[a]Five or more determinations per value, counting times 16-20 hours (1).
[b]Underlined values from NBS Certificate of Analysis (Information values are those given with no errors.) Other values from various studies (see Ref. 1).
[c]NBS values as in footnote b. Other values from Ref. 3.
[d]One sample, 2.75-hr count.

1079207

Table 2. Concentrations of Elements in NBS Fly Ashes (SRM 1633 and SRM 1663a) and in Oil Shale

Element	SRM 1633		SRM 1633a		Oil Shale	
	PGAA[a]	Other[b]	PGAA[a]	NBS[b]	PGAA[c]	Other[d]
H (%)	-	-	-	-	1.7±0.1	1.50±0.03
B (μg/g)	433±4	434, 493	39.2±0.7	-	76±2	94±2
Na (%)	0.30±0.02	0.32, 0.28	0.21±0.06	0.17±0.01	1.69±0.09	1.71±0.03
Mg (%)	1.5±0.2	1.8, 1.78	-	0.455±0.010	3.62±0.05	3.5±0.1
Al (%)	12.6±0.2	12.7, 12.3	14.0±0.2	14	4.0±0.1	3.8±0.1
Si (%)	21.8±0.3	21, 17	22.2±0.4	22.8±0.8	15.9±1.2	14.2±0.9
S (%)	0.39±0.04	0.44	0.27±0.02	-	0.66±0.06	0.65±0.05
K (%)	1.76±0.05	1.72, 1.61	1.97±0.04	1.88±0.06	1.59±0.06	1.66±0.07
Ca (%)	4.75±0.08	4.7, 4.69	1.29±0.11	1.11±0.01	9.8±0.2	10.1±0.7
Ti (%)	0.72±0.02	0.74, 0.70	0.84±0.01	0.8	0.155±0.010	0.18±0.02
V (μg/g)	190±50	214±8	360±40	300	-	84±14
Mn (μg/g)	480±25	493±7	190±15	190	-	313±7
Fe (%)	6.1±0.1	6.2, 6.7	9.7±0.2	9.40±0.10	1.97±0.09	2.03±0.05
Cd (μg/g)	1.50±0.07	1.45±0.06	1.07±0.05	1.0±0.15	0.7±0.3	0.63±0.02
Nd (μg/g)	62.1±2.4	58, 81	65.6±5.4	-	-	19±2
Sm (μg/g)	12.1±0.4	12.4	16.0±0.2	-	2.8±0.2	3.08±0.07
Gd (μg/g)	17.5±0.3	-	23.5±0.3	-	3.1±0.2	-

[a]Five irradiations of approximately 18 hours each.
[b]Underlined values from NBS Certificate of Analysis (Information values are given without errors indicated.) Other values are from various studies (see Ref. 1 for details).
[c]Two irradiations of 2.5 hours each.
[d]C. L. Wilkerson, Battelle Northwest, private communicaton, 1980.

1079208

Table 3. Concentrations of Boron, Nitrogen and Sulfur in Shale Oils

Element	Above Ground Shale Oil		In situ Shale Oil	
	PGAA[a]	Other[b]	PGAA[a]	Other[b]
B (μg/g)	1.0±0.2	-	0.5±0.2	-
N (%)	1.33±0.05	-	0.83±0.02	-
S (%)	0.81±0.02	0.82	0.71±0.05	0.72

[a]Two irradiations of 18 hours each.
[b]C. L. Wilkerson, Battelle Northwest, private communication, 1980.

Table 4. Concentrations of Sulfur and Vanadium in #6 Fuel Oils

Element	SRM 1634		High Sulfur		Low Sulfur	
	PGAA[a]	NBS[b]	PGAA[c]	Other[d]	PGAA[e]	Other[d]
S (%)	2.21±0.07	2.14±0.02	2.24±0.11	2.3	0.67±0.10	0.5
V (μg/g)	309±11	320±15	420±170	-	-	-

[a]Three irradiations of approximately 18 hours each.
[b]Certified values.
[c]One 1-1/2 hour irradiation.
[d]S values supplied by Potomac Electric Power Company.
[e]One 18-hour irradiation.

B. Volcanic Samples

Some of the most dramatic demonstrations of the value of PGAA have come from our applications of the method to a few representative sampes of volcanic materials (collected under support of other projects funded by NSF and NASA or given to us by other investigators). Yellow deposits are frequently found near volcanoes. Since most such deposits that have been analyzed contain mainly sulfur, investigators have usually assumed that all similar deposits are sulfur. As reported in preliminary form in the 1979 Progress Report and, in more detail in Ref. 4, PGAA quickly revealed that some yellow deposits (and others ranging from white to brown) collected near Mt. Erebus in Antarctica contained little sulfur, ranging from 0.7 to 10.9%. These analyses, augmented by instrumental neutron activation analysis (INAA), showed that the deposits contained large amounts of Na, Al and halogens (Cl and F). In part, previous failures to identify the deposits were probably the result of the fact that we find that they are quite soluble; thus, they are very fragile in the environment under normal circumstances. The very cold, dry environment of the vicinity of Mt. Erebus, however, preserved these deposits. Further investigation of the deposits collected by the Maryland group and Prof. William Rose of the Michigan Technical University, using x-ray diffraction, has revealed several minerals present in the deposits: $FeCl_3 \cdot 6H_2O$ (hydromolysite) and several new minerals, AlF_3, $NaAl_4O_4Cl_5$, and $NaAl_4O_4(Cl,F)_5$.

Following the recent eruptions of Mt. St. Helens in the State of Washington, we were able to collect more yellow deposits before they had an opportunity to be dissolved away. Some yellow deposits are, indeed, mainly sulfur. However, other yellow deposits with slightly different appearances are found to be similar in composition to those discovered at Mt. Erebus.

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Concentrations of representative deposits from Mt. St. Helens, Mt. Erebus and Kilauea in Hawaii are shown in Table 5. Although the first two are not identical, they are similar in that they have substantial concentrations of Na, Al, Fe and halogens and modest amounts of S. By constrast, the Kilauea deposit is the traditional "yellow deposit" associated with volcanoes, being nearly pure sulfur.

The results again demonstrate the special value of PGAA in geochemical studies, as the elements measurable often account for a major portion of the mass of the samples. In Table 5, we see that the measured elements account for 47, 74 and 100% of the masses of the three deposits. Much of the missing mass in the first two samples is probably oxygen. Often one can estimate the mass of the oxygen by expressing the major elements in terms of the masses of their common oxides (e.g., Na_2O, Fe_2O_3, SiO_2), as we've done below. It would probably not be accurate to use that method on these samples because of the unusual nature of the minerals. Much of the missing mass in the first sample may be that of F, which we did not measure. These results demonstrate the need for a reliable, simple method for determining oxygen concentrations, a problem that we address in the proposal for next year's work.

Table 6 shows results of analyses of other volcanic samples. Columns 2 to 6 contain results of analyses of fresh ash samples that fell to the ground at various distances from Mt. St. Helens following the massive eruption of May 18, 1980. The data from Mt. St. Helens show some interesting trends with distance, e.g., increasing concentrations of Si, B, Cl, and K, and decreasing Mg, Al, Ca, Ti, V and Fe. It is beyond the scope of this report to give detailed geochemical and atmospheric transport interpretations of the data. However, these data also demonstrate useful features of PGAA as applied to geochemical samples, in general, and volcanic samples in particular. First,

1079211

since these ashes and lavas undoubtedly consist of rather common minerals (unlike the deposits discussed above), it should be safe to account for the oxygen by taking the sums of the major elements expressed as their common oxides. We have done so and show the results in Table 6. We have included only the oxides of the eight major and minor elements Na, Mg, Al, Si, K, Ca, Ti and Fe in those sums and find that the sums range from about 93 to 101% of the total mass. Second, we have listed the irradiation times at the bottom of Table 6. Although the uncertainties tend to be somewhat greater for the shorter irradiations, we see that those of only two to three hours yield quite useful results. Further improvements in the quality of data available from even shorter runs should become possible when we attach the second detector to our beam line. As it will have no NaI crystal around it, we can move it closer to the detector to achieve higher counting efficiencies, thus reducing irradiation times needed to obtain the same uncertainties as with our present detector.

The third advantage of PGAA as applied to an active volcano is that, if necessary, the analyses can be available with in a few hours after receipt of the samples. Since the spectra are taken during the irradiation, results are available as soon as the spectrum can be run through the data-reduction program on the TP-5000 system, which requires only a few minutes. The quick turn-around time of analyses, which may be important in a rapidly changing situation such as an active volcano, is to be contrasted with the several-week period required for complete INAA studies or several-day periods to dissolve samples, etc. if chemical methods are used.

We are also analyzing samples of suspended particles collected in plumes from Mt. St. Helens with aircraft. A set of samples of the initial eruptive clouds was collected by a NASA U-2 aircraft and analyzed by PGAA. The results

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indicate that the composition of suspended particles in the plume is different from the ash that falls to the ground. As shown in Table 7, there is a definite fractionation of composition versus altitude. For example, the Si/Al ratio increases from 3.7 to 4.4 from 43 to 58 thousand feet. Such a fractionation had been predicted by volcanologists, but until these samples were analyzed by PGAA, no hard evidence for the effect existed. The fractionation is primarily due to the means of production of the ash from the magma and the old rock of the mountain that was broken up by the force of the May 18 explosion.

1079213

Table 5. Results of PGAA Studies on Bright Yellow Deposits from Three Volcanoes

Element	Concentration (% by weight unless noted)		
	Mt. St. Helens (crater)	Mt. Erebus (rim)	Kilauea (1971 fumarole)
H	4.37±0.01	3.62±0.04	-
B (μg/g)	45.4±0.5	10.9±0.2	1.9±0.2
F	-	34±4	-
Na	1.6±0.2	3.08±0.02	-
Al	7.3±0.3	13.8±0.3	-
Si	-	5.2±0.5	-
S	8.5±0.6	0.66±0.03	99.94±0.16
Cl	19.2±0.1	7.01±0.05	-
K	0.39±0.06	1.55±0.05	-
Ca	1.9±0.2	1.71±0.08	-
Ti	0.14±0.03	0.27±0.01	-
V (μg/g)	-	160±40	-
Mn (μg/g)	400±70	1430±20	-
Fe	3.5±0.3	2.91±0.03	-
Cd (μg/g)	<0.05	22.1±0.2	0.07±0.03
Sm (μg/g)	0.54±0.02	8.50±0.02	-
Gd (μg/g)	0.6±0.3	6.3±0.2	-
Total	47%	74%	100%

1079214

Table 6. Analyses of Various Ash and Lava Samples by PGAA[a]

Element	Mt. St. Helens (May 18, 1980 eruption)[b]					Other Volcanoes		
	Yakima (185 km)	Wenatchee (195 km)	Moss Lake (240 km)	Lind (280 km)	Pullman (320 km)	Kilauea lava	Erebus lava	LaSouffriere ash
H (μg/g)	580±90	1380±110	630±110	900±100	900±100	1140±40	405±70	535±100
B (μg/g)	8.4±0.2	15.2±0.2	15.3±0.3	16.1±0.1	16.2±0.2	2.4±0.1	13.0±0.5	14.1±0.6
Na (%)	3.21±0.04	3.24±0.13	3.48±0.13	3.37±0.07	3.46±0.15	1.64±0.04	5.75±0.10	2.75±0.09
Mg (%)	2.2±0.3	1.20±0.10	1.26±0.17	1.1±0.2	0.85±0.15	3.5±0.2	<0.5	2.6±0.6
Al (%)	9.47±0.11	9.06±0.06	8.73±0.07	8.71±0.05	8.94±0.06	6.5±0.1	10.2±0.2	9.6±0.2
Si (%)	27.6±0.3	28.3±0.6	30.0±0.4	30.2±0.2	30.3±0.3	24.1±0.5	25.2±0.3	26.7±0.2
S (μg/g)	<175	3570±150	400±200	570±200	850±70	2800±200	1700±200	<150
Cl (μg/g)	530±20	940±30	950±15	1020±10	1040±10	410±15	1400±40	1830±70
K (%)	0.79±0.02	1.13±0.02	1.29±0.03	1.34±0.04	1.31±0.01	0.39±0.02	3.86±0.04	0.52±0.03
Ca (%)	4.21±0.08	3.63±0.04	3.00±0.04	2.99±0.03	3.00±0.04	7.35±0.15	<1.0	5.7±0.2
Ti (%)	0.511±0.006	0.427±0.005	0.384±0.004	0.383±0.003	0.352±0.003	1.57±0.01	0.591±0.014	0.563±0.005
V (μg/g)	205±25	125±15	150±30	140±20	50±10	<50	110±45	270±70
Mn (μg/g)	805±40	590±10	540±10	560±60	500±10	1250±30	1900±100	1150±120
Fe (%)	4.5±0.2	3.48±0.05	3.04±0.05	3.05±0.11	2.86±0.15	8.10±0.08	3.60±0.04	5.65±0.13
Cd (ng/g)	<70	230±50	80±40	65±33	95±40	70±50	<50	<50
Sm (μg/g)	2.62±0.08	3.21±0.05	3.02±0.03	3.05±0.02	3.11±0.01	5.33±0.01	15.3±0.1	3.37±0.08
Gd (μg/g)	2.5±0.3	2.9±0.2	2.6±0.2	2.7±0.2	2.8±0.2	5.08±0.07	10.8±0.2	4.4±0.5
Irradiation Time (h)	3.3	16	19	44	19	16	1.9	2.0
Total (as oxides)	99%	96%	98%	98%	97%	97%	93-94%	101%

[a]Sample weights ranged from 0.3 to 0.8 g.
[b]Distance of locations from volcano indicated beneath locations.

1079215

Table 7. Concentrations of Elements Borne by Particles in Plume from the May 18 Eruption of Mt. St. Helens

Altitude (ft)	Concentration ($\mu g/m^3$) (STP)			Si/Al
	Si	Al	Cl	
43,000	850	230	4.0	3.97
46,000	740	180	1.5	4.11
50,000	550	130	1.0	4.23
58,000	1100	250	2.2	4.40

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C. Biological Samples

We have begun to explore the use of PGAA as applied to samples of human tissue and fluids and to an unusual type of fish. Dr. Robert Henkin at Georgetown University Medical Center supplied samples of blood, which we freeze-dried prior to analysis. Only one sample was analyzed by PGAA, with results shown in Table 8. At present we have been able to analyze for only the six elements listed. Chlorine is so strongly activated and has so many prompt γ-ray lines distributed over the spectrum that it will be difficult to observe many more elements by PGAA using freeze-dried whole blood. However, as a part of our project on stable-isotope tracers (see Sect. V), we are developing some chemical separation procedures. If we obtain samples from which Cl has been largely removed, we will run them on PGAA to see if additional elements can be observed.

In our stable-isotope study, we are mainly using instrumental neutron activation analysis (INAA) and in Table 8, we compare the results for three of the elements and also list data from the literature. The agreement is quite reasonable among the various sets of data, except for sulfur. However, INAA is not very sensitive for S in this type of sample and it was not observed in two of the four samples analyzed by INAA. Thus, the average of all four samples (from different people) is surely much less than 12 mg/g.

In Table 9 we show analyses of liver samples from a human, from cows and from an Antarctic fish. For most elements, the concentrations of the observed elements are comparable among the three types of liver, usually agreeing within a factor of two. The major exception to this is Cd which is more than order of magnitude higher in the human and fish liver than in the bovine liver. Cadmium is well known to be a cumulative, potentially toxic trace element. In view of the much longer life of humans than cows and the exposure

1079217

of humans to elevated levels of Cd resulting from anthropogenic activities, it is not surprising that the concentration in human livers is much higher.

The Antarctic fish, Dissostichus mawsoni, live deep in the Ross Sea off the coast of Antarctica and appear to be one of the most unique fish in existence. They have very little hemoglobin or other chemical agents in their blood to carry O_2 and CO_2, but instead are believed to depend on the natural solubility of those gases in fluids at the very low temperatures of the Antarctic Ocean. The fish grow to 40-kg mass and are suspected of living to ages greater than 100 years. Our interest in them stems from the possibility of observing bioaccumulation over these very long lifetimes. Since they live in the most pristine water on Earth, it is somewhat surprising that their livers contain Cd in amounts comparable to those of humans, but this may simply be a manifestation of their long lives and accumulation times. If the lifetimes of the fish can be "calibrated" in terms of size or some other feature, one could perhaps use them to observe long-term effects of anthropogenic mobilization of toxic elements by fossil fuel combustion and other industrial processes.

1079218

Table 8. Concentrations of Elements Observed in Freeze-Dried Human Blood by PGAA and Comparisons with Other Data

Element	Concentration (mg/g)[a]		
	PGAA[b]	INAA[c]	Other[d]
H	74.3±0.3 (1)		
C	380±35 (1)		
N	160±5 (1)		
S	5.4±0.5 (1)	12±3 (2)	8.05 (137)
Cl	8.0±0.1 (1)	8.3±1.8 (4)	13.6 (405)
K	7.7±0.2 (1)	7.5±1.9 (4)	7.65 (1275)

[a]Number of samples indicated in parentheses.

[b]Uncertainty represents the expected standard deviation of the analytical measurement and does not incude real sample-to-sample variations.

[c]Uncertainty is the observed standard deviation among the two or four samples.

[d]Based on Ref. 5, which gives concentrations in mg/L of whole blood. We have estimated concentrations in freeze-dried blood assuming a density of whole blood of 1.06 g/ml and that the solid residue contains 20% of the mass of whole blood (based on our observations during freeze-drying).

1079219

Table 9. Concentrations of Elements in Liver Samples as Determined by PGAA

Element	Concentration (dry weight basis for freeze-dried samples)		
	Human Cadaver[a]	Bovine Liver[b] (SRM 1577)	Dissostichus mawsoni[c]
H (%)	9.85±0.11	6.8±0.3	9.48±0.03
B (μg/g)	6.0±1.0	3.2±0.2	4.7±0.5
C (%)	66±3	52±2	64±3
N (%)	13.5±0.1	10.4±0.3	5.7±0.2
Na (%)	0.94±0.02	0.31±0.06	0.39±0.05
Al (%)	0.28±0.05	-	<0.16
S (%)	1.00±0.01	0.72±0.02	0.55±0.22
Cl (%)	0.86±0.01	0.30±0.01	0.47±0.01
K (%)	1.15±0.02	1.00±0.03	0.71±0.02
Fe (%)	0.29±0.07	-	<0.11
Cd (μg/g)	9.6±0.2	0.27±0.06	3.2±0.2
Sm (μg/g)	<0.06	-	-

[a]Obtained from Dr. S. H. Harrison, NBS.

[b]Ref. 1.

[c]Obtained from Dr. Arthur DeVries of the University of Wisconsin; total fish was 1.24 m long and weighed 23.1 kg.

1079220

D. Neutron-Capture Cross Section of Bore Hole Samples

A great deal of work has been done on the use of neutron irradiations in bore holes to learn about the composition of various strata through which the bore holes penetrate. In order to obtain maximum, accurate information from logging of wells, one must have fairly good knowledge of the neutron-absorbing properties of the major matrices around the bore hole. Direct measurements of neutron absorption properties of bulk materials can be made, but often the core samples obtained aren't large enough to do the measurements. Since PGAA is an especially sensitive method for observing elements with high neutron-capture cross sections, it might be much more convenient to use PGAA to measure the concentrations of all elements with high cross sections. As the cross sections for most elements vs. neutron energy are well known, one could perhaps compute the neutron-absorption properties for neutrons of any energy more accurately than they could easily be measured.

We are collaborating with Dr. Joseph Harris of the Sandia Corporation on a test of the hypothesis described above. He is engaged in a study of neutron propagation in rocks and soil related to bore-hole explorations for uranium. He has supplied us with several samples of sandstone, which we have analyzed for the elements observable by PGAA. Table 10 shows results of our analyses of three samples of the same material. There is quite good agreement among the three analyses despite the fact that two of the samples were irradiated for very short times. Independently, Dr. Harris has measured the cross section of the sandstone directly by placing samples of it in the ARMF reactor at Idaho Falls and observing the resultant changes of reactivity. The data are now being analyzed. We plan to continue this callaborative effort into next year as, if it becomes successful, it will represent a large improvement in ones ability to interpret field data.

1079221

Table 10. Concentrations of Elements in Samples from a Sandstone Bore-Hole Core

Element	Concentration			
	Sample 1	Sample 2	Sample 3	Avg.±σ
B (μg/g)	13.59	13.70	13.55	13.6±0.1
Na (%)	1.59	1.50	1.44	1.51±0.08
Mg (%)	<0.37	0.3 (±0.1)	<0.38	0.3±0.1[a]
Al (%)	4.42	4.31	4.28	4.34±0.07
Si (%)	38.1	35.7	36.1	36.6±1.3
S (μg/g)	-	700 (±300)	-	700±300[a]
Cl (μg/g)	45	69	<120	57±17
K (%)	2.06	1.97	2.03	2.02±0.05
Ca (%)	0.53	0.53	0.54	0.53±0.01
Ti (μg/g)	656	605	640	634±26
Fe (%)	<0.23	0.22 (±0.04)	<0.37	0.22±0.04[a]
Cd (μg/g)	1.19	0.89	1.03	1.04±0.15
Sm (μg/g)	2.38	2.19	2.16	2.24±0.12
Gd (μg/g)	2.6	2.6	2.5	2.6±0.1
Irradiation time (hrs)	2.3	20	1.0	

[a]Reflects statistical uncertainty for only Sample #2.

1079222

E. Boron in Semiconductor Silicon

Boron is one of the two most common dopant elements added to high purity silicon in manufacturing of semiconductor devices. Its concentration is not easily measured by conventional trace element procedures, especially instrumental methods. However, PGAA has excellent sensitivity for B; in fact, we have been able to measure B concentrations in nearly every sample ever analyzed on the system. The destructive Doppler-broadened capture γ ray at 478 keV has four interferences, the major one being a Na line at 472 keV that can be resolved by our detector if much Na is present. The accuracy of B determinations is limited principally by uncertainty in the background arising from capture of stray neutrons in the B_4C used to stop neutrons around the beam tube. This background corresponds to about 0.5 μg of B at the sample position.

In order to demonstrate the applicability of PGAA to this class of high purity samples and to aid in the eventual development of standards, we analyzed a series of Si samples doped with B. The samples, in the form of 11-mm diam disks, were obtained from W. R. Thurber of the Electron Devices Divsion of NBS. They had been doped with B in nominal concentrations from 2 to 1000 μg/g. The B concentration in one of the samples, plus a series not included in those we obtained had been measured by the nuclear track technique (6). Concentrations observed in irradiations of 11 to 160 min length are listed in Table 11. There is reasonable correspondence between the measured values and the nominal values, although the latter are not very accurately known. The agreement for the nominally 2 μg/g sample is quite poor; however, this was fortunately the sample measured by the track method, for which the result agrees with ours. Samples 521-65 was supposed to be blank, but obviously it is not. Dow-21 is a true blank, which we find to contain <0.6

μg/g of B. We are expecting to obtain some indirect measurements of the B concentrations taken by another group at NBS using Hall-effect measurements. In the meantime, we have tested the B measurement method by analyzing NBS standard glass (SRM 611), which yielded results in agreement with the accepted value.

This study demonstrates that the system can be used to measure B concentrations down to the vicinity of 1 μg/g. However, if desired, we could push the limit down by at least another order of magnitude if larger amounts of material are available and one is willing to irradiate samples for 12 to 24 hours. Note that, in this study, samples of about 100 mg were used vs. the usual 1 g and that irradiation times were from 11 to 160 min. The lowest B concentration we have reported is 0.24±0.08 μg/g in the USGS rock BIR-1 (North Carolina Diabase) (7).

1079224

Table 11. Concentrations of Boron in Boron-Doped Silicon Samples

Sample No.	Weight (mg)	Boron concentration (μg/g)		
		Nominal	PGAA	Nuclear Track Method
A0.00087B-1	153	1000	753±4	
0.0010B-74-1	93	800	716±4	
0.0018B-73-1	92	500	409±2	
0.0030B-45-1	89	275	245±2	
A0.0042B-1	123	200	166±2	
A0.0061B-1	135	120	118±2	
E0.0092B-1	87	70	72.4±1.1	
A0.014B-1	133	35	41.3±1.0	
0.020B-58-1	85	20	22.5±1.0;21.6±1.5[a]	
0.0548-62-1	85	5	5.3±0.9	
521-57	80	2	11.6±1.5	9.3
521-65	83	0.003	228±2	
Dow-21	92	0	<0.6	

[a]Determinations made six months apart to check for time variations of analysis

1079225

III. RECOMMENDED γ-RAY LINES FOR QUANTITATIVE DETERMINATIONS

For each of the elements detected in any of the samples studied during the course of this project, we have determined the γ-ray lines that are most useful for quantitative measurements. The γ-ray lines of substantial intensities that are free of interference or for which corrections for interferences can be made accurately are tabulated. Possible interference contributions to the γ-ray lines from other elements present in the samples have also been investigated and magnitudes of the intereferences determined. These tabulations have been published in the thesis of Dr. M. P. Failey (Report ORO-5173-008 of this project). Since they occupy 31 tables, some of more than one page, we do not include all of them here. However, we have included some examples of those tables and upon request, we can supply copies of the report or of just the tables to interested persons.

In Tables 12 to 14, we show typical tabulations for the elements Si, S and Fe. They list the recommended γ-ray lines for measurement of each element and include the most intense lines in the standard spectra and the observed count rate of the lines in terms of counts/sec-mg (also called the "sensitivity") as measured from the standard spectra, often for both the singles and Compton-suppressed modes. In cases for which background is significant, the background count rates are listed. There are, of course, directly applicable only to our system; however, they give the user an idea of the background rates to be expected in a system constructed similarly to ours. We have included in the recommended list, γ-ray lines that have substantially lower count rates than the most intense ones, but that have been found to have few interferences and lower general spectrum background beneath the peaks. Mainly, these are high energy γ rays, which tend to have lower sensitivities because of the drop in detection efficiency with increasing energy, but which

1079226

usually occur in much less complex areas of the spectrum than low energy lines.

In addition to the standard count rates, the rates of all measurable background γ-ray lines are listed in the tables for the corresponding elements. The information given in the last column indicates how to calculate the amount of each interference that must be subtracted from the peak in relation to the best observable lines of the interfering species. For example, in Table 12, if one wants to use the peak at 1273.3 keV to determine the Si concentration, the last column indicates that there are potential interferences from Cu, Sm and Gd. To remove the Gd interference, for example, one is instructed to multiply the peak area of the strong Gd peak at 182 keV by 0.0148 to estimate the contribution of the Gd 1270-keV peak to the multiplet. As they presently stand, the count rates and corrections in the tabulations are all specific to our detection system and neutron flux. However, with the knowledge of the flux in our system (2×10^8 n/cm^2-sec) and the detector efficiency curve (in the 1979 Progress Report, Failey's thesis and in a paper submitted to J. Radioanal. Chem.), one can adjust all of the values to absolute emission rates per unit neutron flux and then to count rates in some other system of known flux and detector efficiency.

Throughout the tables, uncertainties of count rates and correction factors are indicated in parantheses. A single digit indicates uncertainty of the last digit of the number to which it is attached and two digits indicate uncertainty of the last two digits of the number.

These tabulations should be of considerable value to the community of researchers doing PGAA work. However, that audience is presently so small, and the tabulations is so bulky that it would probably not be practical to publish it in the open literature at this time. However, as noted above, we

1079227

would be pleased to supply the information to any users who would be interested in it.

1079228

Table 12. Recommended γ-Ray Lines for the Analysis of Si with Observed Standard Count Rates and Possible Interferences

E_γ (keV)	Singles Count Rate (c/sec/g)	Suppressed Count Rate (c/sec/g)	Interferences		
			Element	E_γ (keV)	Magnitude
752.5[a]	0.549 (16)	0.575 (9)	Gd	750	0.0077 (6) x 182
1273.3[a]	3.611 (19)	3.608 (14)	Cu	1273	0.004 (1) x 159
			Sm	1269	0.0012 (3) x 334
			Gd	1270	0.0148 (7) x 182
2092.8	2.901 (15)	2.912 (13)	Cl	2092	0.0303 (3) x 517
			Fe	2091	0.0054 (8) x 352
2235.5[a]	0.228 (8)	0.227 (4)	Cl	2231	0.0033 (3) x 517
				2235	0.0007 (2) x 517
2517.3	1.175 (11)				
2781.2	0.147 (8)	0.156 (4)	P	2777	0.0050 (20 x 637[b]
			Fe	2782	0.0010 (4) x 352
3028.2 (SE)	1.784 (13)	0.354 (6)	Al	3033	0.0494 (5) x 1779
			Cl	3025	0.0009 (3) x 517[b]
3539.2	6.567 (18)	6.515 (16)	C	3531	0.0907 (36) x 1261
			P	3533	0.0159 (16) x 637
			S	3531	0.0025 (2) x 841
			Fe	3531	0.0043 (5) x 352
3911.2 (DE)	1.519 (11)				
4422.2 (SE)	2.374 (16)		C	4434	0.368 (11) x 1261
			Al	4427	0.0048 (12) x 1779
			S	4430	0.0195 (6) x 841
4933.2[a]	4.153 (16)		C	4945	0.633 (13) x 1261

1079229

Table 12 Continued

E_γ (keV)	Singles Count Rate (c/sec/g)	Suppressed Count Rate (c/sec/g)	Interferences		
			Element	E_γ (keV)	Magnitude
5869.2 (SE)	0.476 (6)		Fe	5869	0.0025 (9) x 352
6380.2	0.513 (6)		Fe	6380	0.0048 (10) x 352
6687.8 (SE)	0.292 (5)				

[a]Ref. 8
[b]Singles spectrum only

1079230

Table 13. Recommended γ-Ray Lines for the Analysis of S with Observed Standard Count Rates and Possible Interferences

E_γ (keV)	Singles Count Rate (c/sec/g)	Suppressed Count Rate (c/sec/g)	Interferences		
			Element	E_γ (keV)	Magnitude
840.4[a]	53.52 (8)	53.21 (6)	K	843	0.0327 (13) x 771
			Gd	841	0.0027 (6) x 182
2379.4[a]	14.76 (4)	14.62 (4)	Cl	2383	0.0015 (2) x 517
			Fe	2385	0.0028 (4) x 352
2709.2	1.39 (2)				
2752.9	1.72 (2)	1.69 (2)			
2929.9	4.91 (3)	4.88 (2)	Fe	2926	0.0072 (9) x 352
3219.7[a]	6.68 (3)	6.53 (2)	Fe	3225	0.0066 (5) x 352
3369.6[a]	1.35 (2)	1.38 (1)	Cl	3374	0.0056 (3) x 517
4398.6 (DE)	3.87 (3)		Al	4389	0.0084 (14) x 1779
4909.6 (SE)	6.22 (4)		Al	4902	0.0154 (12) x 1779
			P	4912	0.007 (3) x 636
			Cu	4907	0.0022 (8) x 159
			Sm	4910	~0.0002 x 334
5420.6	8.95 (3)		Si	5409	0.0049 (14) x 1273
			Al	5411	0.0072 (10) x 1779
			Cu	5418	0.0055 (9) x 159

[a]Ref. 8.

1079231

Table 14. Recommended γ-Ray Lines for the Analysis of Fe with Observed Standard Count rates and Possible Interferences

E_γ (keV)	Singles		Suppressed		Interferences		
	Count Rate (c/sec/g)	Background (c/sec)	Count Rate (c/sec/g)	Background (c/sec)	Element	E_γ (keV)	Magnitude
122.0[a]	21.35 (7)	--	21.40 (6)	--		--	
352.3[a]	45.65 (6)	--	45.62 (5)	--	S	352	0.0079 (6) x 841
					Mn	355	0.0033 (7) x 212
					Gd	350	0.0029 (6) x 182
692.0[a]	14.11 (4)	0.0043 (10)	14.11 (4)	0.0043 (10)	Si	694	0.0038 (16) x 1273
					Mn	690	0.0031 (4) x 212
1612.8[a]	8.80 (6)	0.0020 (12)	8.80 (6)	0.0020 (12)		--	
1725.2[a]	10.34 (10)	0.0047 (15)	10.27 (9)	0.0047 (15)	Cl	1730	0.0117 (10) x 517
					Sm	1727	~0.0003 x 334
					Mn	1725	0.0021 (3) x 212
5920.3[b]	3.49 (2)	0.0061 (7)	--	--	Mn	5921	0.0030 (14) x 212
6018.5[b]	3.55 (7)	0.0061 (7)	--	--		--	
6609.1(DE)	5.02 (11)	0.0073 (7)	--	--	Cl	6619	0.0341 (10) x 517
6623.5(DE)	3.92 (11)	0.0067 (7)	--	--	Cl	6627	0.0196 (8) x 517
7120.1(SE)	7.51 (11)	0.0086 (8)	--	--	Cu	7126	0.0425 (16) x 159
7134.5(SE)	6.91 (11)	0.0065 (7)	--	--	Cu	7126	0.0425 (16) x 159
7631.1[b]	7.03 (6)	0.0068 (6)	--	--	Cu	7637	0.0352 (12) x 159
7645.5[b]	5.87 (5)	0.0039 (5)	--	--	Cu	7637	0.0352 (12) x 159
8275.8(DE)	0.59 (1)	0.0003 (1)	--	--		--	
8786.8(SE)	1.00 (3)	0.0009 (3)	--	--		--	
9297.8	0.61 (1)	--	--	--		--	

[a]Ref. 8.
[b]Ref. 9.

1079232

IV. SYSTEM IMPROVEMENTS

A. Beam Filter System

In last year's proposal we indicated the need to place a single-crystal of bismuth in the neutron beam. As described there, thermal neutrons undergo "channeling" through the crystal and are thus attenuated much less strongly than two major sources of background, fast neutrons and γ rays. The γ rays in the beam that are scattered by samples into the detection system cause such a large background below about 300 keV in the prompt γ-ray spectra that we are able to observe only the most intense low-energy capture lines. If the background could be reduced, we would probably be able to observe several additional elements whose most intense lines occur at low energies, especially some rare earths (10).

A bismuth single crystal of the Brockhouse type (11) of dimensions 10-cm long x 3.5-cm diam. was purchased from Atomergic Chemicals Corp., and received recently. In addition, we are in the process of obtaining some quartz crystals that were used for similar purposes at the Lawrence Livermore Laboratory reactor, which was recently shut down. However, before these crystals can be installed in the beam, we must build a cryogenics system to cool them to liquid-nitrogen temperature in order to increase the transmission of thermal neutrons. We had planned to have that done at this time; however, we require the help of the NBS reactor staff in design and construction of the cryogenics and they were unavailable for other tasks while the reactor was being overhauled during the long shut-down that occurred during this year (see Sect. I). However, work is now proceeding smoothly and we expect to have the installation made and tested within a few months.

B. Second Sample Position

The upper beam tube has been modified to accommodate a second sample

1079233

holder and a "singles" Ge(Li) detector. We have found from experiments with our present detection system that the sensitivity could be improved for many measurements by use of a detector without the NaI crystal around it. The absence of the large NaI crystal allows one to improve the counting efficiency of the Ge(Li) detector by moving it closer to the sample. The first experiments with the new sample location will begin as soon as the additional neutron and γ-ray shielding for the second detector is complete. We are hoping to be able to run experiments at both locations simultaneously. However, before doing so, we will first have to determine whether or not neutron scattering by samples at the new location (which is 20 cm below the original sample position) will cause serious divergence at the original position.

C. Data-Handling Facilities

The computer system (built around a Digital Equipment Corp. PDP 11/34 computer) that controls data acquisition and analysis has been extensively modified to permit it ot use a more flexible operating system that will expand the capabilities of the system for taking and analysis of data. The computer system formerly used an operating system called TPOS-I which was supplied by Tennecomp, the builder of the pulse-height analyzer system. The conversion which was done now permits the use of the RSX-11M operating system supplied by Digital Equipment Corp. (DEC). This change means, among other things, that the system can potentially function with two or more video terminals operating on a true time-sharing basis. Unfortunately, the system software generation done at Tennecomp Systems, Inc. was inadequate to provide immediate access via additional terminals. At this stage, Tennecomp declared bankruptcy leaving the conversion incomplete, but usable. Several problems have been encountered with the magnetic-disc and -tape controllers, with the latter as yet

1079234

unresolved. At present, little or no software or hardware support is available from other companies for Tennecomp equipment. However, we are negotiating with DEC regarding the completion of the system as originally intended.

Advantages of the new operating system will include the ability to compile programs in a number of high level languages including Fortran, Basic and Cobol, true time-sharing capability and the ability to use much more sophisticated peak-fitting and data-handling routines. Also, RXS-11M is widely used among the scientific community, especially at the National laboratories, and with some modifications (e.g., the additional of DEC floppy disks) we would be able to exchange data and programs with other groups quite easily.

1079235

V. RELATED PROJECT SPIN-OFFS

The demonstrations of applicability of PGAA and other nuclear aalytical techniques have led to the funding of related areas of research by other funding agencies. In the 1979 Progress Report and proposal, we had performed calculations regarding the possible use of stable isotopes as tracers for in vivo studies in humans, especially persons under age 18 and pregnant women, for whom radioactive tracers cannot be used to study the uptake and metabolism, etc. of trace elements. The calculations shown in the 1979 Report were not very optimistic in terms of the sensitivity of the method and the amounts and costs of enriched isotopes needed per experiment if done by PGAA alone. Since that tune, we have done more detailed calculations that include the use of other techniques (especially INAA and instrumental photon activation analysis, IPAA), as well as PGAA. According to the calculations, most elements can be measured best via a very minor isotope that happens to be strongly activable in INAA, e.g., $^{74}Se(n,\gamma)^{75}Se$, where ^{74}Se has an isotopic abundance of only 0.9% and the ^{75}Se has a 120-day half life, which allows it to be observed long after 15-hr ^{24}Na and other interferences have decayed. It appears quite likely that we are going to receive funding from the U.S. Department of Agriculture Human Nutrition Program for development of stable-isotope tracing for Cr, Zn and Se. If so, the funding of stable-isotope work will be shifted to that project, but we may use PGAA for a part of the measurements. In any case, we will continue to explore the applications of PGAA to biological samples under this project as discussed in Sect. II.C.

The results obtained on volcanic samples (Sect. II.B. and previous work) with PGAA, INAA and other analytical methods are in part responsible for our being received funding from NASA (along with investigators from Drexel

1079236

University, University of Arizona, Dartmouth College and Michigan Technological University) for studies of the atmospheric emissions from volcanoes. Any routine analyses of volcanic samples by PGAA will be supported by that project, but if any very usual samples become available we will investigate them as further opportunities to extend PGAA applications as in the example of the new minerals described in Sect. II.B. No funds for collection of samples are charged against this project. Shortly after the May 18, 1980 eruption of Mt. St. Helens, the NSF announced a special program for rapid funding of scientific studies of it and modest funds were obtained by this group.

1079237

VI. PUBLICATIONS AND ADDRESSES

A. 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).

3. 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).

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1079238

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1079239

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1079240

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1079241

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No. 1910-1400

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DOE/ER/05173-013

RENEWAL PROPOSAL

TO

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

"NON-DESTRUCTIVE DETERMINATION OF TRACE ELEMENT CONCENTRATIONS"

SUBMITTED BY

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College Park, Maryland 20742

Funds requested: $105,135

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

Present Contract No.: DE-AS05-76ER05173

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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.

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1079244

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,

1079245

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.

1019246

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.

1079247

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.

1079248

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).

1079249

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.

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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

1019251

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

1079252

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

1079253

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

1079254

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

1079255

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.

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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

1079257

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.

1079258

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.

1079259

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1079261

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No. 1910-1400

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2. DOE Contract No. DE-AS05-76ER05173

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   - [ ] b. Conference paper:
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DOE/ER/5173-01

RENEWAL PROPOSAL

TO

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

"NON-DESTRUCTIVE DETERMINATION OF TRACE ELEMENT CONCENTRATIONS"

SUBMITTED BY

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College Park, Maryland 20742

Funds requested: $108,300

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

Present Contract No.: DE-AS05-76ER05173

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.

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1079264

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.

1079265

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

1079266

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

1079267

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

1079268

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.

1079269

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

1079270

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

1019211

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

1079272

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

1079273

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

1079274

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.

1079275

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.

1079276

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

1079277

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

1079278

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.

1079279

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1079281

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No. 1910-1400

U. S. DEPARTMENT OF ENERGY

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RENEWAL PROPOSAL

TO

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

"NON-DESTRUCTIVE DETERMINATION OF TRACE ELEMENT CONCENTRATIONS"

SUBMITTED BY

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Funds requested: $110,000

Contract period: December 1, 1982 - November 30, 1983

Present Contract No.: DE-AS05-76ER05173

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1079283

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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.

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1079284

I. INTRODUCTION

One of our major objectives during the remainder of the present budget year and the coming year is the completion of quite a number of projects we have started and publication of the results, especially the analyses of many standard reference materials and rocks.

Last year's work on two key problems of the nuclear energy industry, the measurement of burnable poisons and the assay of heavy element isotopes, was quite successful and we will continue to investigate these applications.

There is considerable interest in the possible use of boron as an atmospheric tracer of emissions from coal-fired power plants. As neutron-capture prompt γ-ray activation analysis (PGAA) is an excellent method for boron analyses, we plan to use it to measure boron in some previously collected coal and fly ash samples, and four separate size fractions of particles collected in the stack of a coal-fired power plant. Furthermore, we will investigate the use of PGAA to observe B concentrations on air-filter samples and in artificially entrained soil.

Now that we have successfully developed matrix-dilution techniques for materials containing high concentrations of elements with large neutron-capture cross sections, we will explore PGAA analyses of a series of glasses.

In cooperation with the National Environmental Specimen Bank, we will investigate the application of PGAA to new classes of biological samples.

One of our major projects for the coming year will be the completion and testing of the ^{252}Cf system for PGAA laboratory studies.

With partial support of Sandia Laboratories, we will develop a library of γ-ray energies and intensities of the various elements.

1079285

II. NBS NEUTRON BEAM FACILITY

A. Nuclear Materials

1. Assay of Heavy Element Isotopes

Last year, we proposed to determine if one could use PGAA to assay various heavy element isotopes which, if successful, might lead to Safeguards applications. As described in this year's Progress Report (Sect. II.B), we have performed measurements on several uranium oxide standards with ^{235}U abundances ranging from 0.5 to 90%, as well as sections of sintered commercial fuel pellets. In the spectra obtained, we have observed weak prompt γ rays from $^{238}U(n,\gamma)^{239}U$ reactions and a multitude of lines from ^{235}U(n,fission) and, possibly, $^{235}U(n,\gamma)$, which are expected to be weak on the basis of previous studies (Weitkamp et al., 1974). Intensities of various lines in the spectra are proportional to the ^{235}U content of the samples, but we don't know their origins. The next job that must be done is the identification of the lines associated with fission products by comparison of spectra taken during and immediately after irradiations. The use of extremely high resolution Ge detectors that have recently become available would help greatly in the unravelling of these complex spectra, which have at least 300 photopeaks below 2 MeV.

We propose to continue these experiments and concentrate on reducing the large mass of data associated with them. In the course of this work, we will determine whether or not it will be necessary to use new experimental techniques (e.g., a beam chopper to observe fission products with sub-second half lives) to assay heavy element isotopes. If we can obtain permission to do so, we would like to irradiate samples containing substantial amounts (several mg) of fissile species other than ^{235}U, e.g., ^{239}Pu, to see if the patterns of fission-product γ rays are sufficiently different (because of differences in the yield-mass curves) that one can use them to determine the amounts of ^{235}U

1079286

and ^{239}Pu present in mixed samples. We have irradiated some very small quantities of ^{239}Pu, but they were too small to yield useful spectra.

2. Burnable Poisons in Nuclear Fuel

Our preliminary studies on the analysis of B_4C-Al_2O_3 pellets (used for control of power reactors during start-up cycles) in cooperation with Dr. Failey of Babcock and Wilcox were very promising (see Sect. II.C of 1982 Progress Report). As demonstrated, PGAA yields quite accurate boron analyses and is probably the easiest assay method available. As some sample preparation is necessary, we have begun to work on pulverization and matrixing methods designed to avoid neutron self-shielding effects caused by the high boron cross section and its high concentration in the pellets as received.

We will perform additional analyses of the spectra obtained from uranium fuel containing added Gd. It is difficult to observe Gd lines because of the complexity of the fission-product spectra from the uranium.

B. Environmental Samples

1. Atmospheric Boron

As described in the 1982 Progress Report (Sect. III.A.2), concentrations of boron in coal fly ash are huge, up to 2000 ppm. We suggested there that boron might serve as a very sensitive marker for atmospheric particles originating from coal-fired plants. However, at present almost nothing is known about B concentrations on the suspended particles that leave coal-fired plants via the stacks. Gladney et al. (1978) did PGAA of cascade-impactor samples collected from the Chalk Point power plant in Maryland, but the masses of particles collected in the various size fractions were so small that they could observe B only on the back-up filter, which collects particles of diam <0.5 μm. The B concentration in that size fraction was about 2 $\mu g/m^3$ of stack gases, whereas that of Al (Gladney et al., 1976) is of the order of 200 $\mu g/m^3$.

1079287

As Al comprises ~10% of the mass of fly ash, we estimate that the B concentration in the particulate mass in that size fraction is ~0.1% or ~1000 ppm. It should be noted that the precipitator fly ash at Chalk Point contained only 33 ppm B, so if our crude estimate is correct, there was a large enrichment of boron between the ash that remained in the plant and that which escaped. If this is true, the B concentrations might reach percent levels on particles from plants in which the precipitator ash contains >1000 ppm B.

As PGAA is an ideal method for observing B, we proposed to analyze the coal, precipitator fly ash and suspended particles collected from the stack of a western coal-fired plant. We have contacted Dr. John Ondov of Martin-Marietta Laboratory in Baltimore, who has indicated that he can supply gram quantities of suspended particles in four size fractions ranging from 2-μm diam to 20-μm diam, as well as coal and precipitator ash. The special value of these samples is that they come from a plant that has been thoroughly studied in many ways, including INAA studies of the composition of the coals, ash and suspended particles, x-ray diffraction studies of the numerals in stack samples, mutagenic studies, etc. (e.g., Ondov et al., 1979; Hansen et al., 1981).

Very little is known about concentrations of boron in the atmosphere, as there is no convenient method for measuring it. Because of the importance of such measurements, we plan to explore the possible use of PGAA for that purpose. In previous studies we have observed absolute masses of B as small as 0.25 ng. This limit of detection would probably be small enough to allow us to observe boron on typical air-filter samples collected in urban areas. However, we cannot be certain that this is the case, as the boron peak is so broad (Doppler-broadening) that our ability to see it depends strongly on the general background level in the 480-keV region of the spectra, which is in

1079288

turn dependent on the hydrogen concentration in the sample. If we cannot observe B in typical air filters, we will collect high volume samples on Teflon filters to reduce the hydrogen from the filters themselves. If this is not successful, we will attempt other methods, e.g., placing filters against plastic detectors sensitive to the charged particles released in the $^{10}B(n,\alpha)^{7}Li$ reaction. Another possibility would be that of placing semiconductor detectors or ion chambers near the samples in the beam; however, we would like to avoid that method, as it would require the use of a vacuum chamber. If a successful technique can be developed, we would then do a small survey of atmospheric boron concentrations in the Washington, D.C. area. If these results are interesting, we will apply to EPA for support of a more extensive study.

2. Composition of Suspended Dust

We plan to continue studies on the fractionation of elemental compositions of dust suspended in the laboratory settling chamber described in Sect. II.F of the 1982 Progress Report. Clearly we can determine concentrations of 17 elements in the bulk soil by PGAA, plus about 20 additional elements by INAA. We are now ready to attempt analyses of the separate size fractions collected from the chamber with a cascade impactor. This will be difficult because of the small masses of material that will be collected. If these analytical measurements are successful, experiments on suspension and analysis of particles from dust collected around the world will be performed under support of another agency (NOAA or NSF).

3. Chesapeake Bay Colloids

We will continue the exploratory PGAA studies of colloidal material separated from Chesapeake Bay waters by Prof. Jay Means of Chesapeake Biological Laboratory (see Sect. II.I of 1982 Progress Report). If we are

1079289

able to analyze the small amounts of material that can be separated for enough elements that are of interest in the chemistry of natural waters, we will attempt to continue the study under support of other agencies.

C. NBS Coal Standard Reference Materials

We will soon complete the analyses of the new coal standards, SRM 2682 to 2685 (in collaboration with Dr. R. M. Lindstrom of NBS). While these will be certified as engineering standards, major and trace element data are often valuable in coal-related studies requiring this kind of standard. As pointed out in the 1982 Progress Report, PGAA is a reliable method for determining sulfur and 15 or so other elements.

D. Geological Samples

1. Bore-Hole Samples

We plan to continue our collaborative effort with Dr. H. Bivens and Dr. J. Harris of Sandia Laboratories in the evaluation of bore-hole samples and related standards. By correlating our elemental PGAA analyses with Sandia's total cross-section measurements on the same samples, the Sandia group is developing a model for *in situ* measurements of the compositions of rocks around the bore holes at various depths. Such *in situ* measurements would be made by lowering a 14-MeV neutron generator and Ge(Li) detector into the bore hole. This system, if it can be successfully developed, will give far more definitive information about the compositions of wall rocks than is now obtained by conventional well-logging procedures. The implications of such a system in searching for petroleum, uranium and many other mineral resources are enormous.

2. USGS and NBS Rock Standards

As described in Sects. II.E and III.B of the 1982 Progress Report, we are making excellent progress on the analyses of the two NBS rock SRMs and the

1079290

17 USGS standard rocks. We plan to complete the analyses very soon and publish the results.

3. New Geological Samples

We plan to evaluate some geological standards that recently became available: a series of Canadian reference soils and the International Atomic Energy Agency (IAEA) standards SOIL-1 and SL-1 (Lake Sediment). The PGAA technique has the advantage of allowing us to observe the major crustal elements and, in the case of soils, we may be able to observe the C and N concentrations, as well as the important trace elements B and Cd.

E. Organic and Biological Samples

1. Total Chlorine in PCB Standard Reference Material

We are collaborating with the NBS staff in the certification of two new SRMs for polychlorinated biphenyls (PCBs). They are to certify the total Cl concentration in these SRMs, but have been having difficulty doing so with instrumental neutron activation analysis (INAA) because of the loss of volatile species of Cl after irradiations. The PCBs themselves are viscous liquids of high molecular weight and not very volatile. However, Szilard-Chalmers effects following prompt γ-ray emission can release the Cl atoms from their original bands. We felt this project would be a good opportunity to demonstrate one of the advantages of PGAA with respect to INAA, namely the fact that the prompt γ rays are emitted in such short times after neutron capture that there is no opportunity for the newly formed atom to move away. After the prompt γ rays have been observed in PGAA, it doesn't affect the results if the species is lost from the sample.

Our initial experiments with the PCBs, however, brought to our attention the problem of measuring Cl in organic matrices discussed in the 1982 Progress Report (Sect. II.D). Briefly, the apparent concentrations of Cl measured by

1079291

PGAA are about 10% too high if the sample contains a several percent concentration of hydrogen (vs. a standard containing little H). As soon as we complete our investigation of that problem we can easily determine the Cl concentrations of the PCB standards.

2. National Environmental Specimen Bank Samples

In the 1981 Progress Report we described our cooperation efforts with people from the National Environmental Specimen Bank at NBS to develop PGAA methods for the analysis of human liver samples. In work supported mainly by EPA (to NBS), the PGAA system has been used to analyze a number of liver samples for H, B, C, N, Na, P, S, Cl, K and Cd (Harrison et al., 1981). During the coming year, they will be collecting two new types of environmental samples: mussels from coastal waters of the U.S. and some kind of grain (not yet determined). We plan to explore the use of PGAA on these types of samples.

3. IAEA Biological Standards

As described in Sect. II.E of the 1982 Progress Report, we are in the midst of analyzing the IAEA biological samples, Animal Blood and Cellulose. The PGAA work is essentially complete, as well as INAA for short-lived species (not listed in the Progress Report). We will finish the INAA for long-lived species and report the results within a month. In addition we plan to evaluate the new IAEA standards V-8 (Rye Flour), MA-A-1 (Copepod Homogenate) and H-4 (Animal Muscle) in order to add to the rather sparse data now available on them.

4. Boron Uptake by Cells

We plan to investigate the use of PGAA for the measurement of boron doped into human cells. Dr. Harry Hadd of the University of Indiana-Gary will collaborate on this "first-look" experiment. He is working on B neutron-capture work for the purpose of cancer therapy, and wishes to measure the uptake of this element by $\sim 10^7$ cells in a culture to which the B solution is

1079292

added. This could hopefully lead to the determination of optimum B-doping levels for various types of malignant tissues. If cancerous tissue in a living subject could absorb boron and then be subjected to neutron-irradiation, this treatment could, perhaps, preferentially destroy the malignancy.

F. Industrial Samples

As we feel that PGAA has many potentially important industrial applications, we occasionally analyze samples for which PGAA might be especially useful. (From discussions with people from many industries, we find that they are not very interested unless one has already demonstrated the system's analytical capabilities with their particular kinds of material.) In last year's proposal we indicated our interest in analyzing a series of commercial glasses. We began the work this year, but encountered the problem that many glasses contain elements of high cross sections, which was the reason we expected PGAA to be especially applicable to them. However, concentrations of these elements, especially B and Cd, are often so great that neutron self-shielding is a very serious problem. Because of that, we stopped work on the glasses. In the meantime, we have been working on the burnable poisons project (Sect. II.A.2 above and Sect. II.C of the Progress Report), in which we encountered the same problem with B_4C-Al_2O_3 pellets. In the work on that project, we developed methods for handling such materials, including pulverizing the samples and mixing the powder quite thoroughly with powered graphite, which dilutes the high cross-section material enough that we can make reliable PGAA studies. We plan to return to the glass study soon by use of this method.

G. Archeological Samples

We plan to finish the PGAA measurements on pottery shards from Alexandria, VA, and from New Jersey soon and publish the results (see Sect. II.H of 1982 Progress Report).

1079293

H. Equipment Changes

1. In-Beam Flux Monitor

We are considering installation of an in-beam flux monitor in the NBS system. Presently we irradiate a Cr monitor once per day in the sample position, which yields variations of up to 3% due to sample geometry and flux changes. Some sort of permanent and accurate on-line, real time measurement of each sample would reduce our systematic errors significantly. One possibility would be the use of Rh wire near the sample position, as neutron capture forms a 45-sec pure β-emitter, which would come into equilibrium after a few minutes of irradiation. As it emits no γ rays, it would not increase the background and one could monitor the current resulting from the β emission. Such a system has been used successfully at Livermore.

2. Additional Data Handling Facilities

As noted in the 1982 Progress Report (Sect. V), we have received funds totaling $98,000 from NSF and the University to upgrade our data-acquisition and -treatment facilities. Specifications have been written for the equipment and we are now awaiting the long approval process of the State of Maryland that is unfortunately required for all purchases of computer-related equipment. As soon as the equipment is installed, we should be able to process data from this project much more rapidly than at present.

3. High Voltage Power Supplies

We have been supplying high voltage power to our Ge(Li) detectors with battery packs for a number of years. The deterioration of the capacitors has reached the point where we must replace these units. As detectors are much better able to withstand loss of power and commercial electronic power supplies more reliable and less noisy, we will use electronic replacement units.

1079294

4. Shielding and Mounting for the ^{252}Cf Source

We expect to try several different arrangements for the mounting and shielding of the ^{252}Cf source. A number of items are available from the dismantling of the cylcotron but construction and machining will be required.

1079295

III. ^{252}Cf-BASED SYSTEM

A. Set-Up and Tests of ^{252}Cf Facility

We plan to continue the development of the laboratory PGAA system based on the ^{252}Cf neutron source (see Sect IV.B of 1982 Progress Report). We now have a graduate student working on the project and have worked out the computer-interfacing for the multichannel analyzer that will be used at the source and have personnel shielding in place for our prototype system (described in the 1982 Progess Report). We now need to construct shielding for the Ge(Li) detector before making the first measurments on real samples and standards. Then we will pursue two lines of work:

1. Use the existing prototype to determine compositions of interesting samples of several types (e.g., geological, industrial, biological) to test the value of such a system if it were placed in a laboratory or industrial environment.
2. We will work toward an optimal design of the source, shielding and detector configuration by a combination of experiments with simple geometries and calculations of neutron transport and energy spectra, the latter in collaboration with Mr. Ray Hoover here at the University, or with the Sandia Laboratories group. After these experiments are complete, we will build a more permanent set-up.

B. ^{252}Cf-Based Measurements on Small Sources

Dr. Jack Trombka of NASA-Goddard has made PGAA experiments using very small sources (1-10 μg) of ^{252}Cf and very large "samples", e.g., brick walls. As we have a small source (in addition to the 150-μg source), we plan to measure prompt γ-ray spectra from a variety of very large samples.

1079296

IV. HIGH RESOLUTION SPECTRUM

As noted in Sect. IV.A of the Progress Report, we attempted to irradiate a sample of NBS SRM 1633 Fly Ash at the Grenoble (France) reactor in order to obtain a very high resolution γ-ray spectrum up to about 2 MeV using their bent-crystal spectrometer. The experiment was terminated because of problems with the reactor, but the reactor is now operating and people there will put the sample on and run it. We will receive a magnetic tape containing the data and do the analyses here.

V. PROMPT GAMMA-RAY LIBRARY

There is a great need for a reliable "library" of prompt γ-ray spectra of the elements. We had hoped that other workers would compile such a library, but the latest one (Lone et al., 1981) has many errors and it contains many listings from Rasmussen et al. (1969) which we have found to suffer from inclusion of impurity lines in the "pure" element spectra as well as having occasional errors of γ-ray energies of more than 1 keV. We intend to begin consolidation of much of our data on elemental standards into a prompt γ-ray library and, if there are serious gaps, run spectra of additional elements. We expect to receive partial support for this work from Sandia Laboratories.

1079297

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1079298

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1079299