2up

NASA TECHNICAL MEMORANDUM

NASA TM X-71519

NASA TM X-71519

N74-20335

(NASA-TM-X-71519) TRACE-ELEMENT ANALYSIS
OF 1000 ENVIRONMENTAL SAMPLES PER YEAR
USING INSTRUMENTAL NEUTRON ACTIVATION
ANALYSIS (NASA) 25 p HC $4.25 CSCL 18H

Unclas
G3/24 34351

TRACE-ELEMENT ANALYSIS OF 1000 ENVIRONMENTAL SAMPLES PER YEAR USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

by Dean W. Sheibley
Lewis Research Center
Cleveland, Ohio 44135
March 1974

ABSTRACT

The technology and methods developed at the Plum Brook Reactor to analyze 1000 samples per year and report data on as many as 56 elements are described. The manpower for the complete analysis of 20 to 24 samples per week required only 3 to 3.5 hours per sample. The solutions to problems encountered in sample preparation, irradiation, and counting are discussed. The automation of data reduction is described. Typical data on various sample matrices are presented.

TRACE-ELEMENT ANALYSIS OF 1000 ENVIRONMENTAL SAMPLES PER YEAR USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

by Dean W. Sheibley
Lewis Research Center

SUMMARY

The objectives of the work described in this report were to develop the capability of analyzing a large number of pollution related samples using instrumental neutron activation analysis and to report on a large number of elements with minimum resources expended (manpower, money, and equipment) per sample.

The methods and techniques are described from which an initial capability of six samples per week requiring 10 hours per sample and producing data on 16 elements evolved into the optimum capability where 20 to 24 samples per week required 3.0 to 3.5 manhours per sample and produced data on up to 56 elements.

E-7724

INTRODUCTION

The Environmental Research Office (ERO) of Lewis Research Center requested that the Plum Brook Reactor (PBR) staff develop an instrumental neutron activation analysis (INAA) capability to support a large air particulate sampling program (~650 samples/yr) for the Cleveland metropolitan area.

The effort grew to include support work for the Environmental Protection Agency (EPA), Division of Air Surveillance at Research Triangle Park, North Carolina (260 samples/yr), and the Erie County Health Department at Sandusky, Ohio (25 samples/yr).

There were four goals for the INAA program at the NASA PBR:

(1) Develop the technology and methods to analyze 1000 samples per year (encompassing a variety of sample matrices)

(2) Determine and report data on as many elements as possible

(3) Establish and maintain a high degree of accuracy and precision using INAA

(4) Perform the work with a minimum of manpower and equipment, basically as a part-time effort

This report describes how the program was established to meet these goals. Information is provided on the scheme and the manpower required to perform tasks related to the irradiation and counting of approximately 20 samples per week. Then the problem of data reduction and its automation are discussed. For information purposes, some typical results are presented on various sample matrices.

The reactor capability has been described in NASA Lewis Research Center News Release 72-21. This news release is included as an appendix.

PROBLEM DEFINITION

The initial goal was to develop an INAA capability to analyze 12 samples per week within a man-hour effort of ~60 hours. The capability was to be developed using existing reactor facilities and laboratory counting equipment.

PROBLEM SOLUTION

Capability Development

The work of Dams et al. (ref. 1) and Zoller and Gordon (ref. 2) was used as the basis for building the INAA capability. The INAA procedure they used involved these steps. The sample aliquots were encapsulated in polyethylene vials for the irradiation period; after irradiation the samples were immediately removed from the vials for counting upon return from the reactor core. Two aliquots of the sample plus two standards were irradiated in a pneumatic transfer irradiation system, one set (sample plus standards) for a long time (12 to 24 hr) period, and the other for a short time (5 min) period. The short-time irradiation was counted after decay intervals of 3 minutes, 30 minutes, and 24 hours. The long-time sample was counted after a decay interval of 3 weeks; sometimes the decay intervals were 7 to 10 days. The typical neutron flux was 10^{13} per square centimeter per second. Counting data were processed through computerized data reduction codes. Twenty to thirty elements were reported.

Several major differences existed between this scheme and one compatible with the PBR facilities. The PBR did not have an operating pneumatic transfer irradiation facility, nor was there a sophisticated gamma ray spectrum analysis and data reduction computer program available. Irradiation facilities at PBR were hydraulic. Aluminum capsules (rabbits) were used to contain and transfer samples to and from the core.

The use of aluminum rabbits meant that data on the short-lived elements obtained from the 5-minute decay count would be lost. Significant personnel radiation exposures were obtained from handling the aluminum rabbit (~50 g) directly from the reactor core due to the 1780 keV gamma of 2.2 minute Al^{28}. A remote method used to open the rabbit took too much time (in excess of 20 min).

High density polyethylene proved to be an acceptable rabbit material. With a 2.5-millimeter-thick wall, it adequately withstood the 1.1×10^6 newton per square meter (160 lb/in.^{2}) hydraulic pressure of the irradiation transfer system. The material did not significantly degrade in the PBR core for periods up to 1 hour. Activation of the polyethylene impurities was slight. The rabbits could be opened manually upon return from the core.

We now had acceptable rabbits for the short-term (polyethylene) and long-term (aluminum) irradiations. Since the internal volume of this rabbit design was cooled by primary cooling water flowing through the rabbit, samples were protected by encapsulation in polyethylene and quartz vials for the short- and long-term irradiations, respectively.

Since decay time was critical to the determination of elements from the 5- and 30-minute decay counts, we decided to use the rabbit irradiation facilities with the highest thermal neutron flux to build up the specific activity of short-lived isotopes. The higher flux also provided a greater sensitivity.

Evaluation of PBR Capability

To evaluate our overall capability at this point, ten particulate samples from ERO, collected on Whatman-41 filter paper were encapsulated, irradiated, and counted. Results on 16 elements were manually calculated. The average time expended per sample was 10 hours.

The entire process was then examined to identify those parts of the process which could be improved. This examination resulted in significant manpower savings and more elements reported.

The analysis scheme for the ten evaluation samples used two aliquots (~25 cm^2 of filter paper per aliquot). One aliquot was encapsulated in polyethylene and irradiated in a polyethylene rabbit for 5 minutes in a thermal neutron flux of approximately 10^{14} newtons per square centimeter per second. This sample was counted at decay times of 5 minutes, 30 minutes, and 24 hours. The other aliquot was encapsulated in high purity synthetic quartz and irradiated in an aluminum rabbit for 12 to 24 hours. These samples were counted twice, after decay periods of 10 days and 3 weeks. Sample counting equipment included one 4096 channel gamma ray spectrometer and a Ge(Li) detector.

The Ge(Li) detector had a crystal diameter of 35 millimeters and a length of 27 millimeters. It had a nominal active volume of 20 cubic centimeters, an efficiency relative to a 7.6 by 7.6 centimeter (3 by 3 in.) sodium iodide crystal of 3.65 percent at 1332.5 kiloelectron volts, and resolutions of the 1332.5 kiloelectron volt photons of 2.18 (full width - half maximum) and 4.09 keV (full width - 0.1 maximum). Counting losses at 20 percent dead time were about 6 percent.

The data in the analyzer memory was dumped on 8 channel paper tape, converted to punched cards, and processed through a rather primitive computer program which provided both a count per channel output plus a not too reliable routine for peak finding and integration of net area. All results were hand calculated from net peak areas and theoretical nuclear data parameters. Standards were not used since they increased the number of items to be irradiated and counted. Sixteen elements were reported.

Manpower Analysis

Examination of the 10 manhours per sample showed the following:

(1) One-half hour was required to cut filter aliquots, load into vials, and seal and leak check vials.

(2) One hour was needed for the 5-minute irradiation and counting after decay intervals of 5 and 30 minutes.

(3) One quarter man-hour was necessary for each count after decay intervals of 24 hours, 10 days, and 3 weeks.

(4) The long-term irradiation operation procedure required only one-quarter man-hour for seven samples.

(5) Eight hours were required to hand calculate the data on 16 elements from computer calculated net areas. (The hand calculations were performed on programmable electronic calculators.)

Within the 60 man-hour goal, only half of the desired number of samples had been analyzed. Evident shortcomings of the process were that the number of short-term irradiations per week was apparently limited by (1) the available analyzer counting time and (2) the manpower needed for data reduction. These two parts of the analysis scheme were attacked to improve efficiency. The objective was to increase the number of short-term irradiations and counting in an 8-hour shift as well as to significantly reduce the man-hours for data reduction.

Solving the increasing number of short-term irradiations was simple: Irradiate two samples in the same rabbit, taking advantage of the higher specific activity during long decay times. The first sample was counted after 5 minutes of decay and the second sample immediately after the first 10 to 12 minutes of decay. The 30-minute decay counts were performed after a decay time of 22 to 25 minutes on the first sample and after 40 to 45 minutes on the second sample. Thus, short-term irradiation sample output was doubled while adding only approximately 0.25 hour to the original time interval of 1 hour for one sample. All counting was performed on the same analyzer.

Data Reduction

The data reduction problem required that a reliable computer data reduction program compatible with an existing IBM 360 model 67 computer facility be found.

The literature identified various codes: INVEN by Dams and Robbins (ref. 3), GAMANAL by Gunnick and Niday (refs. 4 and 5), and SPECTRA by Borchardt et al. (ref. 6). INVEN could not be obtained in complete form. GAMANAL, though probably the best of the three codes, was written for the CDC 6600 computer and would require an extensive rewrite to get it on the IBM 360. SPECTRA, though not too sophisticated, was used for this work. The peak find, peak integration, and peak identification properties were used as written. We inserted the equations we used for hand calculations, since the code calculated results based on comparisons with standards. These equations also permitted accurate corrections for dead time losses, decay during counting time, etc. A library of standards was added to the code based on elements in the various sample matrices. The standard library eventually included 56 elements calculated from approximately 80 isotopes. The rewrite, program debugging, and irradiations of standards for the library took 7 months to complete.

Improved Capability at PBR

Twenty-two air particulate samples were analyzed to again evaluate the analysis scheme. The total time for sample analysis averaged 4.5 hours per sample. Two hours of the total were used for checking computer input and results. Up to 56 elements were reported. At this point the initial goal had been achieved. We could analyze 12 samples per week with approximately 54 hours expended.

We continued to push for a more efficient operation. All isotope interference corrections, except for the aluminum correction on magnesium, were computerized. This resulted in more manpower saved in data reduction. By using routine scheduling of both long- and short-term irradiations and counting, we eventually achieved an optimum situation on both manpower and counting equipment availability. This optimum situation permitted analyzing 20 to 24 samples per week with a total manpower of 3 to 3.5 hours per sample expended.

Figure 1 shows the final scheme in use at the time the program was terminated. (The PBR ceased operation in January 1973.) Each operation is identified by a letter in parentheses. Table I provides information on the manpower breakdown for each identified operation. This scheme shown in figure 1 was used for all NAA samples. Results on the pollution related samples went to the Environmental Protection Agency (EPA), Division of Air Surveillance at Research Triangle Park, North Carolina, and the Environmental Research Office (ERO), NASA Lewis Research Center.

A few comments should make figure 1 more understandable. The sample aliquot used for the 5-minute irradiation was sealed in a polyethylene vial, leak tested, and irradiated for 5 minutes. The other aliquot was flame sealed into the Suprasil quartz vial, leak tested, and irradiated for 3 to 12 hours depending on the type of sample. The counting data from each aliquot were punched on paper tape. This tape served as the permanent record of the counted aliquot. Input data, including the sample number and the requestor's identification number, were compiled. The input data and counting data were transferred onto magnetic tape after conversion to a format compatible with the IBM 360 computer. The output from the SPECTRA code consisted of a listing of all input data, counting data, and results, plus plots of the gamma ray spectrum of each sample count. In addition, EPA data listings contained a summary sheet of input data and results for data transmittal. The ERO summary of results was stored in data sets in 360 storage. These results were edited for errors and refiled for use in other ERO data reduction computer programs by using a computer terminal. Table II shows the 56 elements reported in each decay time group.

Other Alternatives to Sample Processing

The 20 to 24 samples per week was considered the optimum since complete analysis of that number of samples could be completed in 5 days, working one $8\frac{1}{2}$ hour shift per day.

We evaluated other alternatives. Another irradiation scheme which showed promise required performing 30 to 36 short-term irradiations during 1 week with the number of long-term irradiations per week increased and held for counting 3 weeks later. This approach involved longer range scheduling, was less routine, and resulted in less efficiency when unexpected reactor shutdowns occurred. It was used occasionally to reduce sample backlogs.

Problem Areas

While developing the INAA capability, many techniques evolved primarily from the types of samples submitted for INAA. The original samples received from ERO were air particulates collected on filter paper. However, as the work grew to include EPA and others, the following types of samples were received for analysis: kerosene, jet fuel, gasoline, coal, fuel oil, residual oil, various ores, bottom ash, fly ash, clam tissue, corn, stack scrubber water, crab shells, river sediment, and river water. The same techniques and methods described in figure 1 were used with slight modifications. For these materials, no significant matrix effects were found.

Another problem we encountered was the impurity content of the filter paper used in the high volume samplers to collect the particulate samples. The conventional filter material used was Fiberglas. However, Fiberglas was not compatible with INAA because of its high and varied impurity content. Discussions with K. Rahn of the Ford Reactor at the University of Michigan revealed that Whatman-41 filter paper was the most desirable filter medium for use with INAA (see ref. 1). Our blank determination for ERO showed Whatman-41 to be very low in impurities with no significant change in impurity level from batch to batch. This work helped establish Whatman-41 as the standard filter in the Cleveland parallel network and the Erie County sampling network for trace element determinations.

Impurity levels were also important in the quartz and polyethylene vials. During the long irradiation time in quartz, the samples decomposed to the extent that complete removal of the sample from the vial for counting was impossible. The samples had to be counted in the vials. We eventually determined that Suprasil (Suprasil T-20, 6 mm i.d., 8 mm o.d.; Supplier, Amersil, Inc., Hillside, N.J.), a synthetic quartz, best served our needs for a low impurity vial material. The irradiation of volatile fuels for EPA required that we also determine the impurity level of polyethylene, since liquid samples were counted in the irradiation vials. We found that impurity levels varied somewhat from batch to batch of polyethylene. Polyethylene was also susceptible to picking up radionuclides from the primary coolant. This interference was eliminated by sealing the sealed polyethylene vials into heat shrinkable tubing. The shrinkable tubing was easily removed after the sample was irradiated.

The problem of flame sealing gasoline and other volatile materials into quartz for the long irradiation was solved by the use of a cold finger condenser in liquid nitrogen (LN_2). The quartz tube (about one-half full, 0.8 cm^3) was positioned in an aluminum rod which had been bored out to accommodate the length of the tube from its bottom to above the liquid level. This rod was then lowered into a dewar containing LN_2 and allowed to stand until the gasoline became slushy and/or a ring of frost appeared just above the top of the aluminum. Then the tube was sealed using an oxygen-acetylene flame. This process took less than 5 minutes.

Accuracy of Computerized Results

With the entire data reduction scheme computerized, the accuracy of results depended on finding errors in the paper tape data and predata input parameters before loading the magnetic tape into the IBM 360 computer (see identification letters H and I in fig. 1). Considerable man-hours were saved because after the SPECTRA analysis of the magnetic tape data was executed errors could be corrected and the SPECTRA analysis re-executed using a computer terminal before the data was erased from the active memory of the computer.

SPECTRA CODE

The computer program SPECTRA (ref. 6) contained an adequate peak find, peak integration, and peak matching routine. The code also distinguished between two types of peaks based on the statistical significance of the γ-ray count data. The code resolved doublets and triplets using a minimum peak area of five channels. This degree of resolution was found to be adequate for almost all peaks used. SPECTRA also contained an option called G-search. The G-search routine was used to estimate the concentration of elements not found during the peak find and matching routine. The code then examined the energy region where γ-ray peaks should be located and provided three estimates of the element concentration.

These features of the code were left intact. We did write into the code a library of standards which was used in lieu of irradiation and counting of standards along with the samples. To establish our working standards, we used spectra of typical sample matrices. Element concentrations were calculated from nuclear data. We substantiated the elemental values of these matrix standards by comparison with homemade or NBS standards. Where discrepancies of >20 percent existed, the data was examined, the problem identified, and corrective action taken. From this we concluded that for these types of samples no significant matrix effects were present. We retained the original standards data tapes and occasionally reran them to check for error in the automatic data processing equipment and software.

Since four decay counting times were used, four standard libraries were used, each with decay time boundaries (see table II). In each library set at least two elements were calculated from two standards each. These two standards represented different concentrations, counting geometries, dead times, decay times, and sample matrices. Visual inspection of the computer listing provided a rapid spot check for computer program malfunctions. Table II shows that one element of each standard pair has an asterisk. The * indicated that the particular standard had a smaller standard deviation associated with the counting data. The element concentration calculated from this standard was selected by the computer as the value printed in both the ERO and EPA summary data sets and listings.

Another problem area involving accuracy was related to linearity of the analyzer-detector system. SPECTRA control integers were adjusted to allow only a three channel variation in gamma ray peak energy to ensure proper peak matching with standard peak energies. The linearity of the analyzer-detector system was checked daily with Cs-137 and Co-60 sources. (The activity of these sources produced dead times in the analyzer-detector system of less than 10 percent.) However, linearity drift did occur. And gain shifts in linearity occurred when sample activities were too high. When the linearity did shift more than three channels, peaks did not match with standards or possibly could be improperly matched. A linearity adjustment subroutine was added to SPECTRA to correct for nonlinearity or drifting of the analyzer system. The subroutine provided information on the true location of six peaks over the energy range which could reasonably be expected in a given decay time group. The search area for each peak was restricted to a given number of channels. The width of the search area increased as the γ-ray energy increased. (This was characteristic of nonlinear behavior of the analyzer-detector system.) A least squares fit of the difference between true energy and actual energy location of at least four peaks was used to derive coefficients for a linear equation. The actual peak locations were then mathematically relocated to a more true energy location before the peak matching routine with the standards was performed. This subroutine virtually eliminated missed peaks or improper peak matches. This saved considerable manhours per week since peaks not matched with standards had to be manually identified and hand calculated.

Examination of table II also shows that some elements were calculated from the same isotope in different decay groups and other elements were calculated from different isotopes in the same or different decay groups. This duplication was used to improve accuracy.

Interference corrections for one isotope on another were added to SPECTRA as subroutines (see table III for corrections used). The correction factor was normally derived from nuclear data tables and then checked with homemade standards of various concentrations. Some correction factors were determined empirically, e.g., the correction for Al^{28} on Mg^{27}. More complex interference corrections were resolved empirically by using two level factorial experiments to evaluate correction coefficients. An example of the correction of Hg for Se-Yb interference is given in reference 7.

Samples which were counted in polyethylene and quartz vials required corrections for the impurity content of the vials. Standard libraries of vial and blank filter paper correction factors were added to SPECTRA. We used indicators in the input data to each computer calculation to call out the proper correction library. The code used corrections for polyethylene vials, Suprasil vials, Whatman-41 filters (25.8 cm^2), and combinations. The computer also did not print the value for an element in a sample, if the microgram quantity was within two times the microgram value of the blank(s). The value output was listed as < the blank value (corrected to proper units). With this restriction, some data were lost. But this restriction eliminated reporting very small values which resulted from the small difference between two larger numbers.

PRECISION AND ACCURACY

As a comparative measure of accuracy, we continually checked out results with homemade standards, NBS standards, and by participation in roundrobin analyses with NBS-EPA.

Table IV presents a comparison of PBR results with four NBS standards containing approximately 60 elements in glass. With the exception of the cobalt result in the NBS 610 standard, the agreement of PBR results with standards is generally good. Typically accuracy was within ±25 percent of the NBS value.

Tables V, VI, VII, and VIII present data on the precision of the instrumental method in four different matrices. The results are taken from an NBS-EPA roundrobin analysis of coal, fly ash, gasoline, and fuel oil. Only data on elements definitely identified as being present are shown. An examination of the data for coal and fly ash reveals that certain elements (for example, Sb and La in table V, Sn and Yb in table VI) have large percent standard deviations, but a small percent range of counting precision. This could indicate that these elements are not homogeneous with respect to that sample matrix.

Table IX shows typical element concentrations of particulates collected on Whatman-41 by the Erie County Health Department in Sandusky, Ohio. Results are given in units of nanograms per cubic meter (ng/m^3) of air filtered.

Table X presents data on the impurity levels in Whatman-41 filter paper. Results are shown as micrograms per 25.8 square centimeters (4 $in.^2$). These values represent averages of 12 batches of Whatman-41 paper. Impurity levels typically did not vary more than ±25 percent from the mean. These values were used in the SPECTRA library.

Table XI provides information on the impurity level of Suprasil synthetic quartz. Weights of impurities are expressed in micrograms (μg) based on a vial 5 centimeters long having an inside diameter of 6 millimeters and outside diameter of 8 millimeters and a weight of 2.77 grams. The data varied significantly from one batch to another for some elements. As a result, the SPECTRA library required revision when a new batch was used. The element which changed most significantly was antimony (Sb).

Table XII presents average results on impurity levels of 16 polyethylene vials. Vial length was 5 centimeters with a 6 millimeter inside diameter and a 9 millimeter outside diameter. The average weight of the sealed vial was 2.00 grams. High density polyethylene was used because of its better radiation resistance. The high impurity levels in these vial blank for S, Na, Cl, K, Al, and Ca severely limited the sensitivity to these elements in gasoline and other volatile materials which had to be counted in the vials.

For example, if the volatile sample plus vial gave a chloride value of 9.4 micrograms, the Cl value output by the computer for the sample would be <9.0 micrograms (referring to Cl in table XII) rather than the difference of 0.4 microgram. If the sample plus vial gave a chloride value of 20 micrograms, the value output by the computer would be 11 micrograms.

CONCLUDING REMARKS

Four goals were realized for the pollution related instrumental neutron activation analysis program at the NASA Plum Brook Reactor:

(1) Develop technology and methods to analyze a large number of various matrices per year - the capability was geared for 1000 samples per year

(2) Determine and report as many elements as possible, up to 56 elements were routinely reported

(3) Establish and maintain a high degree of accuracy and precision using the INAA method, precision was normally <±25 percent, and accuracy was estimated at <±50 percent

(4) Perform the work with a minimum manpower effort and a minimum of equipment (analysis of 20 to 24 samples per week, 3 to 3.5 man-hours per sample, and only one analyzer-detector system)

These goals were accomplished near the end of 1972. The methods used to achieve these goals involved analyzing samples in large numbers; carefully planning and scheduling sample preparation, irradiation, and counting; complete automation of the data reduction scheme by computer; and strict attention by the work team to small details of the overall scheme to avoid rerunning samples because of equipment or method malfunction or data input errors.

This work was terminated in January 1973 when the Plum Brook Reactor was closed.

APPENDIX

A 60-megawatt nuclear test reactor at the NASA Lewis Research Center's Plum Brook Station is playing a new role to help others solve local environmental problems.

The reactor, which is 10 years old, is used to study the effects of radiation on materials and components being considered for space nuclear systems of the future. Now it is being put to work as well on such projects as analyzing trace elements in the air, samples of coal, and other fuels, and even corn damaged by birds.

A method called neutron activation employs the reactor for detecting trace elements such as mercury, arsenic, cadmium, and nickel. The method is based on the simple fact that such substances, when irradiated with neutrons, give off characteristic gamma rays which can be detected and analyzed. Thus the identity of the element and how much of it is present can be determined.

Plum Brook scientists began doing the analyses for Lewis' Environmental Research Office which is assisting the City of Cleveland in identifying and cataloging trace elements and compounds in the air. They have developed special techniques such as flame-sealing volatile samples in quartz vials so lengthy irradiation can be made, and obtained the IBM-360 computer program, SPECTRA, for data reduction. The computer program permits three samples to be processed in the time it originally took to process one sample. The computer program is capable of determining 50 elements from the gamma ray spectra of an irradiated sample.

These advanced techniques have led to requests from other government agencies and colleges to have samples irradiated for their environmental studies.

The Environmental Protection Agency, the prime Government agency working on pollution control, asked Plum Brook scientists for irradiations on samples of coal, gasoline, jet fuel, fuel oil, crude oil, fly ash, and coal products. In all, the scientists are reporting data on some 19 trace elements of concern to the EPA.

The scientists also are irradiating and analyzing samples of air particulates from six sampling stations near Sandusky for the Erie County Health Department; air samples from the City of Oberlin requested by Oberlin College; and samples of the Sandusky river water, sediments from the river, and clam tissue requested by Heidelberg College.

In addition to assisting others in their pollution research, the scientists are irradiating kernels of corn for the Department of Interior's Bureau of Sport Fisheries and Wildlife. Bureau researchers discovered that ears of corn pecked by the birds have grown slightly larger than other corn. So they want to know the affected corn's trace element composition to see if it has the same nutritional value as the other.

REFERENCES

1. Dams, R.; Robbins, J. A.; Rahn, K. A.; and Winchester, J. W.: Nondestructive Neutron Activation Analysis of Air Pollution Particulates. Anal. Chem., vol. 42, no. 8, Jul. 1970, pp. 861-867.

2. Zoller, W. H.; and Gordon, E. E.: Instrumental Neutron Activation Analysis of Atmospheric Pollutants Utilizing Ge(Li) γ-Ray Detectors. Anal. Chem., vol. 42, no. 2, Feb. 1970, pp. 257-265.

3. Dams, Richard; and Robbins, John A.: Nondestructive Activation Analysis of Environmental Samples. COO-1705-6; Rept. 48, Michigan University, May 1970.

4. Gunnick, R.; and Niday, J. B.: Computerized Quantitative Analysis by Gamma-Ray Spectrometry. Vol. I: Description of the GAMANAL Program. UCRL-51061, Univ. of California Radiation Lab., Mar. 1, 1972.

5. Gunnick, R.; and Niday, J. B.: Computerized Quantitative Analysis by Gamma-Ray Spectrometry. Vol. II: Source Listing of the GAMANAL Program. UCRL-51061, Univ. of Calif. Radiation Lab., Dec. 6, 1971.

6. Borchardt, G. A.; Hoagland, G. E.; and Schmitt, R. A.: SPECTRA - A Computer Program for Gamma Ray Analysis. Jour. Radioanalyt. Chem., vol. 6, 1970, pp. 241-271.

7. Sheibley, Dean W.: Trace Element Analysis of Coal by Neutron Activation. NASA TM X-68208, 1973.

TABLE I. - OPTIMUM MANPOWER BREAKDOWN FOR 20 SAMPLES/WEEK

Operation	Identification[a]	Average manhours/ sample
Preparation, encapsulation	A	0.25
Preparation, encapsulation	B	.25
Irradiation	C	.1
Irradiation	D	.1
Counting	E	.25
Counting	F	.55
Counting	G	.25
Data handling	H	.1
Data reduction	I	.8
Data handling	J	.8
Data handling	or K	or 0.3
	Total	3.0 - 3.5

[a] See figure 1.

TABLE II. - DECAY GROUP LISTING OF ELEMENTS AND ISOTOPES USED IN SPECTRA LIBRARIES; ELEMENTS LISTED IN DATA SUMMARY

Decay time group	≤15 min	>15 min ≤100 min	>100 min ≤5000 min	>5000 min	
Elements or isotopes	Al^{28} *Al^{28} Ca^{49} Cu^{66} Rh^{104} S^{37} *S^{37} Ti^{51} *Ti^{51} V^{52} *V^{52}	Ba^{139} Br^{80} Ca^{49} *Ca^{49} Cl^{38} Dy^{165} *Dy^{165} Ge^{75} I^{128} In^{116m1} *In^{116m1} Mg^{27} Mn^{56} *Mn^{56} Mo^{101} Na^{24} Ni^{65} Rb^{88} Sn^{123} Sn^{125m} Sr^{87m} *Sr^{87m} Te^{131} U^{239}	As^{76} Au^{198} Br^{82} Ce^{143} Cd^{115} Cu^{64} Eu^{152m1} *Eu^{152m1} Ga^{72} Gd^{159} Ir^{192} K^{42} *K^{42} La^{140} Mo^{99} Na^{24} Pt^{197} Re^{188} Sm^{153} *Sm^{153} W^{187}	Ag^{110m} Ce^{141} Co^{60} *Co^{60} Cr^{51} *Cr^{51} Cs^{134} Eu^{152}(1408 keV) Fe^{59} *Fe^{59} Hf^{181} *Hf^{181} Hg^{203} Lu^{177} Nd^{147} Ni(Co^{58}) Rb^{86} Sb^{124} *Sb^{124} Sc^{46} *Sc^{46}	Se^{75} Sn^{117m} Ta^{182} Tb^{160} Th(Pa^{233}) *Th(Pa^{233}) Yb^{175} Zn^{65} Zr^{95}
Element listed in computer summaries for EPA and ERO	Al Rh S Ti V	Ba Ca Cl Dy Ge I In Mg Mn Na Sr Te U	As Au Br Cd Cu Eu Ga Gd Ir K La Mo Pt Re Sm W	Ag Ce Co Cr Cs Fe Hf Hg Lu Nd Ni Rb Sb Sc	Se Sn Ta Tb Th Yb Zn Zr

*Smaller standard deviation associated with this standard.

()Refer to isotopes or energies of isotopes used for element.

TABLE III. - INTERFERENCE CORRECTIONS FOR VARIOUS ISOTOPES

Element/ isotope (X)	Interfering isotope (Z)	Correction required
Cu^{64}	Na^{24}	NA(511 keV X) - 0.0886(NA 1369 keV Z)
Hg^{203}	Se^{75}	NA(279.1 keV X) - 0.3866(NA 264.4 keV Z)
Zn^{65}	Sc^{46}	NA(1115.4 keV X) - 0.7767(NA 889 keV Z)
Ce^{141}	Fe^{59}	NA(145.4 keV X) - 0.36(NA 1292 keV Z)
Br^{82}	Mo^{99}	NA(776.5 keV X) - 0.34(NA 740 keV Z)
*Mg (grams)	Al (grams)	Grams Mg calculated - 0.057 (grams of Al)
**Hg^{203}	Yb^{175}, Se^{75}	See reference 6

*This correction was determined empirically, but not programed into SPECTRA; all others were.

**Correction coefficients used were determined from a two level factorial design.

(NA refers to net area of peak.)

TABLE IV. - COMPARISON OF NBS STANDARD REFERENCE MATERIALS WITH PBR RESULTS (PPM)

[NBS values in parentheses are interim values. Others are certified values.]

	NBS 610/PBR	NBS 612/PBR	NBS 614/PBR	NBS 616/PBR
Antimony	---	---	(1.06)/1.1±0.1	0.078±0.007/0.12±0.02
Cerium	---	(39)/37±2	---	---
Cobalt	(390)/135±14	(35)/31±1	0.73±0.02/0.59±0.006	---
Europium	---	(36)/26±1	0.99±0.04/1.1±0.6	---
Gold	(25)/20±2	(5)/4.7±1	(0.5)/1.0±0.8	---
Lanthanum	---	(36)/35±15	0.83±0.02/<2	---
Thorium	---	37.6±0.09/31.2±1	0.746±0.007/0.58±0.15	0.025±0.004/0.018±0.002
Scandium	---	---	0.59±0.04/0.68±0.23	0.026±0.012/0.020±0.004
Silver	(254)/180±80	22.0±0.8/31±7	0.46±0.02/0.57±0.07	---

TABLE V. - PRECISION ON NBS-EPA ROUND ROBIN COAL SAMPLE

Element	Mean (ppm)	$\pm 1\sigma$ (ppm)	Percent standard deviation	Counting precision range (percent) at 1σ
Al	15 700	1550	9	0.6-1
As	5.9	0.5	9	10-12
Au	0.146	0.048	33	10-40
Br	20	3	15	9-12
Ba	337	42	12	5-8
Ca	4070	560	14	8-15
Ce	17 340	0.089	2	1-2
Cl	750	75	10	2
Co	5.48	0.15	3	1-13
Cr	19	0.8	4	3-5
Cs	2.55	0.06	2.3	8-10
Cu	14.1	0.9	6	3-5
Dy	0.85	0.06	7	2
Eu	0.312	0.037	12	0.2-0.3
Fe	7517	119	2	1
Ga	5.4	0.8	14	11-15
Ge	70	5	7	35-50
Hf	0.92	0.05	6	5-10
Hg	0.95	0.09	10	25-33
I	2.78	0.38	14	12-30
In	0.04	0.01	25	20-35
Ir	2.48	0.27	11	5-12
K	3500	360	10	3-4
La	11.3	3.3	30	6-12
Lu	0.416	0.017	4	5-8
Mg	980	250	26	12-33
Mn	38.0	2.6	7	0.5
Na	370	33	9	2-3
Nd	6.4	1.5	24	40-55
Rb	19	1.9	10	10-20
Sb	6.4	1.6	24	8-15
Se	3.8	0.51	13	25-33
Sm	1.3	0.19	15	2-5
Sn	125	20	16	10-15
Sr	93	9.2	10	8-11
Ta	0.360	0.028	8	15-20
Tb	0.03	0	0	0.5-7
Th	3.1	0.2	8	2-20
Ti	1312	150	12	10-20
U	0.980	0.078	8	8-12
V	36	4	11	5-10
W	1.9	0.8	40	30-80
Yb	0.55	0.04	8	15-20

TABLE VI. - PRECISION ON NBS-EPA ROUND ROBIN FLYASH SAMPLE

Element	Mean	±1σ (ppm)	Percent standard deviation	Counting precision range (percent) at 1σ
Al	109 600	4020	3.7	0.6-1
As	69.5	7.6	11	8-10
Ba	2734	167	6	6-8
Br	12.1	1.5	12	35-50
Ca	41 000	3600	8.8	7-16
Ce	129	10	7	2-10
Cl	185	44	24	10-40
Co	38.6	3.7	9	1-10
Cr	122	12	10	2-4
Cs	13.8	1.4	10	8-12
Cu	142	9	6.2	3-4
Dy	7.6	2.4	31	1-8
Eu	2.42	0.16	6.6	1-2
Fe	52 780	5600	11	1
Ga	38.3	6.3	16	8-20
Ge	476	166	35	---
Hf	7.62	0.56	7.3	3-20
Hg	3.7	1.1	30	15-30
In	0.156	0.035	23	33-50
Ir	18.6	3.3	18	8-10
K	21 800	2400	11	3-4
La	77	8	10	3-8
Lu	3.8	0.5	14	5-8
Mg	15 970	8060	50	15-33
Mn	466	31	6.6	0.3
Na	2658	129	4.9	1-2
Rb	115	15	13	8-14
Sb	12.08	0.86	7	10-15
Sc	27.5	2.4	9	0.5-4
Se	12.7	1.8	15	20-30
Sm	10.05	0.58	5.8	2-3
Sn	740	210	28	8-20
Sr	869	33	3.8	5-8
Ta	2.74	0.25	9	15-20
Tb	0.22	0.04	16	3-6
Th	25	2	8	2-3
Ti	8900	752	8.5	10-12
U	8.40	0.56	6.7	8-15
V	230	10.6	4.6	5-7
W	12.7	1.1	8.8	30-50
Yb	6.2	3.4	55	3-25
Zn	700	220	31	10-30
Zr	640	140	22	25-35

TABLE VII. - PRECISION ON NBS-EPA ROUND ROBIN GASOLINE SAMPLE

Element	Mean (ppm)	±1σ (ppm)	Percent standard deviation	Counting precision range (percent) at 1σ
Br	128	10	8	1
Ca	8	4	50	30
Cl	80	6	7	2
Cu	2.3	0.2	8	10-12
Dy	0.0066	0.0020	31	15-40
S	335	44	13	25-40

TABLE VIII. - PRECISION OF NBS-EPA ROUND ROBIN OIL SAMPLE

Element	Mean (ppm)	±1σ (ppm)	Percent standard deviation	Counting precision range (percent) at 1σ
Au	0.0245	0.0007	3	15
Br	0.24	0.07	30	35-40
Ca	15	2	15	---
Cl	18	0.7	4	---
Co	0.25	0.01	4	1-20
Cr	0.116	0.035	30	8-30
Cu	0.22	0.02	10	---
Fe	12.4	1.6	13	5-12
Hg	0.022	0.015	66	10-33
Mn	0.19	0	--	8-12
Ni	39.5	2.26	6	3-7
S	20 400	3900	19	15-20
Sb	0.0146	0.0033	23	16-33
Se	0.19	0.03	17	25-30
V	266	18	7	2-3
Zn	0.48	0.12	25	15-40

TABLE IX. - ERIE COUNTY AIR SAMPLES

Date of sampling: 5/24/71

ng/m^3

Element	Sandusky sewage plant	Castalia fire station	Huron high school	Milan high school	Sandusky high school
Al	5600	2800	3200	540	2200
Ca	4800	2000	2700	1000	3000
Fe	2900	2200	2100	280	2000
K	1800	1100	1200	260	950
Mg	<1000	<1000	1700	560	<300
Cl	960	1000	600	640	900
Ti	620	210	400	64	150
Na	580	2300	480	300	750
Zn	310	1300	172	120	250
Mn	210	200	150	11	160
Br	75	42	51	28	100
Cu	56	49	47	14	9.5
Be[a]	39	36	48	10	30
Cr	34	65	43	~2	32
Cd	<30	<80	<50	<30	<50
V	11	4.9	7.3	0.90	5
Se	7.6	6.0	5.9	1.8	7.0
Rb	5.3	4.4	3.8	0.77	3.7
Nd	5.0	<2	3.0	<1	1.6
Ce	<5	<5	<8	<3	<2
Sb	3.6	3.4	6.2	1.3	3.2
I	<3	<2	<2	<0.5	2
Ce	2.5	1.7	3.1	~0.3	1.5
La	2	<2	2	<0.8	4
As	1.0	7.0	6.5	3.3	8.0
Sc	0.92	0.55	0.65	0.082	0.65
Co	.90	.55	.62	.11	.60
Th	.75	.44	.51	.082	.47
Hg	.67	.24	.19	.16	.20
Cs	.58	.42	.50	.065	.51
Hf	.50	.20	.21	~.01	.23
Sm	.34	.18	.24	.05	.20
Dy	.29	.11	.20	.030	.15
Tb	.27	.28	.17	.04	.16
Lu	.095	.062	.11	.02	.070
Eu	.087	.057	.062	.012	.057
In	~.06	~.1	~.1	.04	.16

[a] Determined by emission spectroscopy.

TABLE X. - IMPURITY LEVEL OF WHATMAN-41 FILTER PAPER

[Micrograms per 25.8 cm^2 (4 in.^{2})]

Element	μg/25.8 cm^2	Element	μg/25.8 cm^2
Ag	0.0088	Fe	1.57
Al	1.03	Hg	.0046
Ba	.049	Mn	.018
Ca	3.5	Na	3.38
Ce	.026	Sb	.0046
Cl	3.23	Sc	.0016
Co	.0022	Ti	.15
Cr	.051	U	.00067
Cu	.08	Zn	.601
Dy	.00009		

TABLE XI. - TYPICAL IMPURITY LEVELS OF A 2.77 g SUPRASIL VIAL

Element	μg	Element	μg
Au	0.00035	Hg	0.00059
Ce	.003	Sb	.01
Cr	.0144	Sc	.0014
Co	.0012	Ta	.00017
Fe	.52	Zn	.092

TABLE XII. - IMPURITY LEVELS IN A 2.00 g POLYETHYLENE VIAL

Element	μg	Element	μg
Al	3.6	In	0.0003
Au	.009	K	9.4
Ba	.48	La	.037
Br	.25	Mn	.046
Ca	4.5	Na	8.1
Cl	9.0	S	162.
Cu	.27	Ti	.95
I	.062	V	.016

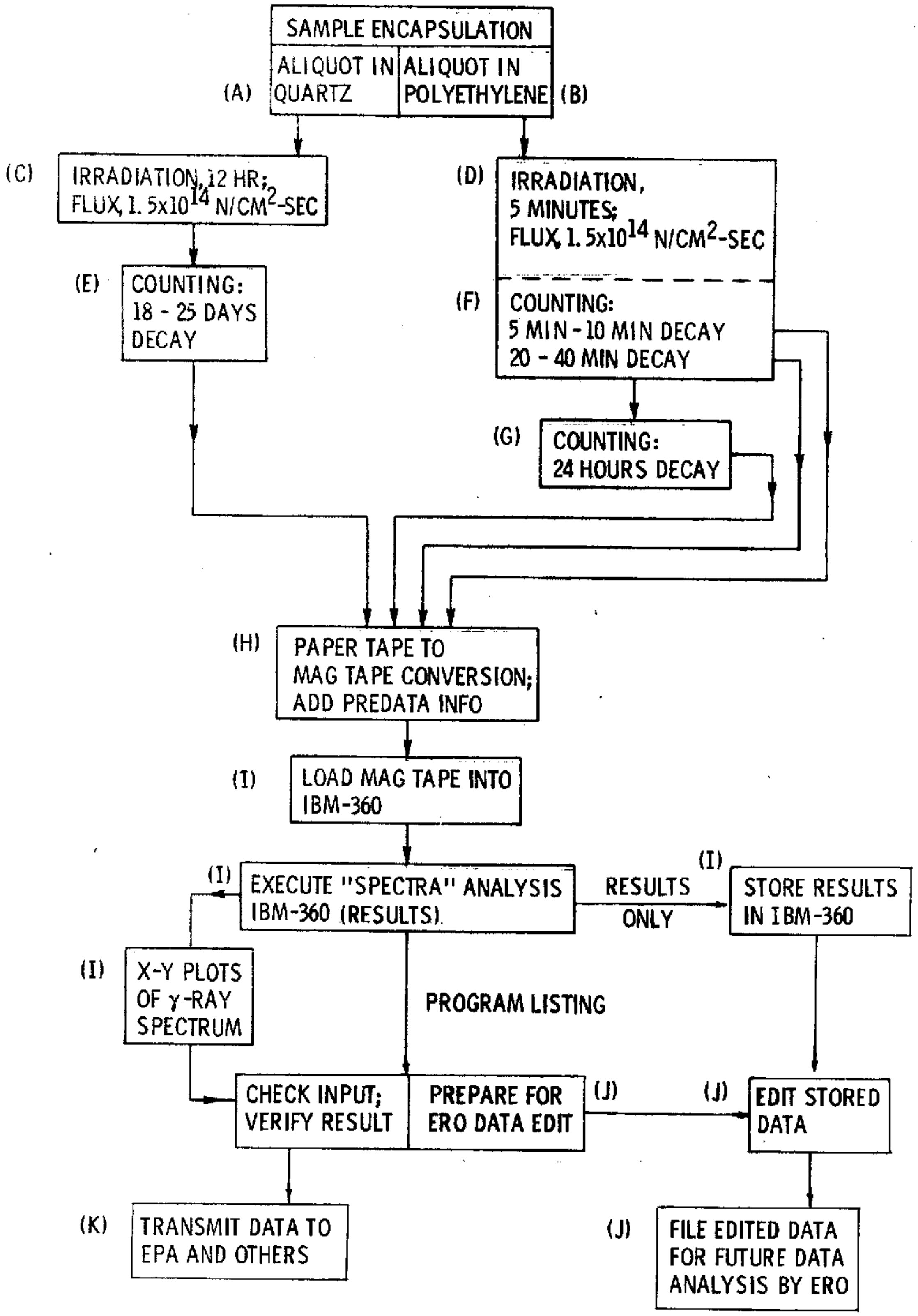

Figure 1. - Flow chart showing scheme for sample irradiation, counting, and data reduction of various samples.