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**METHODS FOR PREPARING COMPARATIVE STANDARDS AND FIELD SAMPLES
FOR NEUTRON ACTIVATION ANALYSIS OF SOIL**

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METHODS FOR PREPARING COMPARATIVE STANDARDS AND FIELD SAMPLES FOR NEUTRON ACTIVATION ANALYSIS OF SOIL

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One of the more difficult problems associated with comparative neutron activation analysis (CNAA) is the preparation of standards which are tailor-made to the desired irradiation and counting conditions. Frequently, there simply is not a suitable standard available commercially, or the resulting gamma spectrum is convoluted with interferences. In a recent soil analysis project, the need arose for standards which contained about 35 elements. In response, a computer spreadsheet was developed to calculate the appropriate amount of each element so that the resulting gamma spectrum is relatively free of interferences. Incorporated in the program are options for calculating all of the irradiation and counting parameters including activity produced, necessary flux / bombardment time, counting time, and appropriate source-to-detector distance. The result is multi-element standards for CNAA which have optimal concentrations. The program retains ease of use without sacrificing capability. In addition to optimized standard production, a novel soil homogenization technique was developed which is a low cost, highly efficient alternative to commercially available homogenization systems. Comparative neutron activation analysis for large scale projects has been made easier through these advancements. This paper contains details of the design and function of the NAA spreadsheet and innovative sample handling techniques.

Introduction

Neutron activation analysis (NAA) brings great power to bear on a variety of matrices. Its usefulness has been demonstrated for materials such as biological tissue including plant matter, geological materials such as ores and rocks, plastic, and for complex matrices such as soil. Recently, a project called the Background Soil Characterization Project (BSCP) was undertaken to determine a variety of organic, inorganic and radioactive analytes in soil that was thought to be relatively free of anthropogenic contamination.¹ The goal was to establish benchmark concentrations for several substances in typical uncontaminated soil. These values could then be

used to gauge the level of contamination of other soils for the purpose of environmental remediation and monitoring. This information would also be useful in tracking the migration of various species in soil.

In the BSCP project, about 35 trace elements were determined by NAA. One major objective in this work was to develop a suitable procedure for the preparation of field samples and comparative NAA standards. It was important to devise a method that would be applicable to batch processes involving medium to large numbers of samples and to include provisions for sample homogenization. Low detection limits were also a high priority for the project.

In order to meet the regulatory requirements of the customer, a major goal of the project was to perform the analyses according to the quality assurance plan dictated by the United States Environmental Protection Agency's Contract Laboratory Protocol (CLP). This plan dictates the use of spiked, duplicate, and blank samples as well as laboratory control samples and continuing calibration verification standards.² Adherence to the CLP resulted in the analysis of approximately one quality control sample for every two field samples.

The comparative method of activation analysis was chosen as the one most likely to be adaptable to the CLP protocol, which was originally designed for atomic spectroscopy techniques. Though other methods of analysis are available, it was thought that the comparative method could most easily satisfy any regulatory concerns. This decision made it necessary to design standards which would yield the least complicated gamma ray spectra and meet a number of other acceptance criteria. The method that was developed for multielement determinations in soil is an extension and refinement of one that was described previously.^{3,4} The comparative neutron activation analysis method, has been thoroughly described in the literature (ref. 5 for example).

Standards must be prepared with analyte concentrations adjusted to yield gamma spectra with photopeaks of individual elements having adequate counts, and thus acceptable counting errors, and yet not be too large as to produce Compton distribution that would interfere with other photopeaks. Also, great care must be taken prior to irradiation to avoid contamination. Lastly, for best results, these standards must closely match the matrix of the samples to be analyzed. Of the many methods for preparing standards, the addition of known amounts of solutions to high purity silica gel powder has many advantages.⁶ High purity silica does not activate appreciably by thermal neutrons, and commercially available products have trace element impurities that are, with one or two exceptions, one percent or less of those found in typical soils. Coupled with the fact that high purity silica can approximate a volume of soil and thus closely simulate the irradiation and counting geometries of the actual samples, high purity silica gel seemed the ideal choice for a standard support.

A common problem with soil analyses is that of sample homogeneity. A finely divided dry powder is normally desired but sometimes difficult to obtain. Contamination before irradiation must be avoided or known so that corrections can be made. Sample throughput also becomes an issue in medium and large projects in which simple mortar and pestle homogenization methods cannot keep up with sample analysis load. A novel method of obtaining an uncontaminated finely divided soil, and innovative methods for preparing soils and comparative standards for multielement analysis was developed and is discussed in this paper.

Experimental

Field samples of the BSCP project were obtained from areas in Anderson and Roane counties in Tennessee and were prepared in such a manner that the possibility of contamination prior to irradiation was minimized. The samples were dried over night in clean polyethylene pans on a table in the laboratory, and then transferred to clean polypropylene vials for homogenization. The polypropylene vials were purchased precleaned from Falcon Corporation. An impactor made of high purity quartz was added to approximately fifteen grams of soil in the Falcon vial. The impactor was made by pulling off about 20 mm lengths of a heated 12 mm diameter Supersil rod and fire polishing the ends. Supersil is high purity quartz made by Amersil Inc. The vials containing the soil and the impactor were placed in gallon paint cans. The cans were then placed on a paint shaker and allowed to shake for 10-20 minutes. As the impactor traveled up and down the axis of the vials, the soil was intimately mixed and reduced to a fine powder. The impactor was then removed from the soil prior to sampling. After use, the impactors were cleaned in warm soapy water, 6 molar HNO_3 , filtered deionized water, and acetone consecutively, and then reused. Occasionally, impactors became pitted and were discarded. Sixteen samples could be prepared simultaneously using this method. Soils containing sand or gravel damaged the Supersil impactors and could not be treated by this method. Large numbers of samples have been and continue to be prepared as described in a relatively short amount of time.

In order to minimize the possibility of contamination during sampling, high density polyethylene irradiation capsules were filled by dipping out the soil from the vial with a new, individually wrapped drinking straw. Care was taken not to touch the end of the straw and to use a new straw for each sample. "Blank" samples of powdered high purity silica gel were

prepared using the same homogenization and drinking-straw sampling procedure.

The standards for comparative neutron activation analysis were prepared by pipetting aliquots of previously prepared "working" solutions onto high purity silica gel powder. The working solutions were mixtures of commercially available atomic spectroscopy standards. Three working solutions were employed: one containing elements that form short-lived activities, and two that form long-lived activities - one as chlorides and the other as nitrates to avoid solubility problems. The short-lived standards were dried under a heat lamp whereas the long-lived standards were dried in a desiccator to avoid the loss of mercury and other volatile elements.

Several methods of pipetting the standards onto the silica gel were attempted. Some samples were pipetted into the bottom of an empty rabbit insert (the irradiation containers) and then covered with silica while others were pipetted onto silica directly, and still others were allowed to evaporate in the bottom of the rabbit insert and then covered with silica. In the latter case, the solution became deliquescent and never dried completely. On cold dry days, static electricity became a problem as some of the silica was observed to escape from the inserts resulting in the possibility of analyte loss or cross contamination of other standards. Pipetting the 300 microliter aliquots into an insert which was partially filled with silica and then adding a layer of fresh silica on top after drying was deemed the most successful method.

The desired concentrations of the various elements in the working solutions were determined using a spreadsheet which calculated the counts in the photopeaks of interest for each nuclide. For soil samples, the quantities taken for analysis, the irradiation times, counting times, and source-to-detector distances, which are discussed below, were selected based on previous experience. It was then only necessary to compute the quantities of elements used in the

standards that would yield adequate photopeak counts. The spreadsheet contains a reaction library, irradiation and decay data tables, counting parameters, germanium detector specifications, and nuclear parameters such as cross sections and gamma ray abundances. By selecting a particular reaction and some parameters such as the desired irradiation and counting durations, one is able to determine if the desired counting statistics can be achieved. In this manner, several sets of parameters were investigated with ease. The concentrations of various elements were then adjusted such that sufficient counting statistics were probable. Aluminum, iron, and potassium could not be purchased at concentrations high enough to use as the other analytes were. Therefore, aluminum was added to the inserts as metal disks, and iron as wire. A special solution of potassium with a high concentration was prepared and a suitable aliquot was added to the working solution. The blank values from the homogenized silica were also subtracted from the standards. Both the samples and standards were sealed in polyethylene rabbit inserts by melting the lid to the body with a hot soldering iron.

The field samples were then grouped into batches containing comparative standards, a spiked sample, a duplicate sample, blank, NIST standard reference materials, and a calibration verification sample as specified by EPA Contract Laboratory Protocol (CLP). Three NIST samples were used in the determination of the long-lived radionuclides (Montana Soil (2711), San Joaquin Soil (2709), and Fly Ash (1633a)).

Three irradiations and four counts were made on each sample and standard at the High Flux Isotope Reactor.⁷ For the short-lived radionuclides, a 100 mg sample was irradiated 10 seconds in a thermal fluence rate of $1\text{E}14 \text{ n}/(\text{cm}^2\text{-sec})$ followed by a 20 minute decay before counting. Samples were counted 5 minutes at source-to-detector distances of up to 70 cm.

A second sample was irradiated 60 seconds in three 20-second portions and counted twice - once after 4 days and again after 20 days. In this manner, the medium- and long-lived radionuclides were determined. Data packages were then assembled and submitted to project managers. Independent data validation was also performed.

Results and Discussion

In order to ensure that no significant contamination was introduced into the field samples, the seven homogenized silica gel blanks were analyzed. Table 1 shows all of the elements that were detected in any of the blanks. Column 4 entitled "Number of Samples" shows how many samples contained measurable amounts of these elements. The last column of data refers to averaged detection limits calculated for those samples in which a particular element was not observed. In all cases except hafnium, the amounts of the elements determined in the blank samples were less than 5 percent of the average value determined in the field samples (see Table 4). Hafnium is believed to be present as an impurity in Aldrich silica gel along with chromium. Since the polyethylene irradiation capsules are sealed by melting the lid to the body with a soldering iron, some chromium contamination is unavoidably introduced. The rabbit inserts must be sealed to avoid the loss of radioactive material after irradiation. Except for Hf, all of the elements pass the CLP criterion for blanks.² Table 2 shows the calculated minimum detectable amounts (MDA) in micrograms for those elements which were not detected in blank samples. These MDA are average values for the seven blanks and are calculated by the software program MDA.⁵ The data in these two tables suggests that no significant contamination was introduced by the method.

Examination of an example comparative standard in Table 3 reveals that the concentrations chosen for the various elements are more than adequate in most cases. There are a couple of noteworthy exceptions for cadmium and samarium. There was insufficient cadmium in the standard as evidenced by the poor agreement between the standard amount and the observed amount. The samarium data is affected by gamma ray interference at the 103 KeV line from ^{239}Np . Because there was insufficient samarium in the standard, the peak search program was unable to successfully resolve the spectral overlap from ^{239}Np . Additional samarium and cadmium could be added to standards to minimize this problem. Another important observation that can be derived from the data in Table 3 is that even though our spreadsheet calculated the amounts of the elements to put in the samples, our goal of 1 percent uncertainty was not always achieved. The concentrations of the elements in the standards are being constantly evaluated to better duplicate the field samples. For example, there was insufficient iron in the standards compared to the soils which resulted in problems with some of the spike recoveries.

In order to assess the quality of the data, a discussion of the performance of the NIST Standard Reference Materials (SRM) is necessary. The Environmental Protection Agency's Contract Laboratory Protocol stipulates that all reference materials must be determined to within 20 percent of their certified value in order to be used as a laboratory control sample. All three SRM materials involved in this study were scrutinized in this manner. Table 4 shows the results for SRM 2709, 1633a, and 2711. The concentrations (ppm) of the various elements are average values of at least 4 determinations. Likewise, the uncertainty values are calculated standard deviations of the mean. Some of the values listed in the Tables are NIST recommended values as opposed to certified values and are denoted by "~" in front of the true concentration. It should

be noted that CLP dictates that only NIST certified values be used whenever possible. In this case, there were elements for which no suitable certified material could be found. With the exception of Cd, all of these elements meet the CLP requirement for laboratory controls.

Preliminary data for 137 field samples is presented in Table 5. The mean concentration in parts per million as well as the minimum (min) and maximum (max) concentrations are reported along with an average detection limit. The number of samples column refers to the number of field samples which were above the detection limit for a particular element. Likewise, the detection limit is averaged from the remaining field samples. Note the large standard deviation in many of the elements. This is indicative of large variation in concentration in the soils analyzed. This is probably true for any soil and may have serious implications for the establishment of background levels of some elements.

Conclusions

Several innovative developments have occurred in this NAA study of background levels of trace elements in soils. Perhaps the most beneficial is the use of very high purity plastic vials and quartz impactors to homogenize soil. The technique was used to treat about 150 soil samples and applied to high-purity SiO_2 to demonstrate that no significant contamination was introduced. The use of a spreadsheet to predict photopeak areas and design standards for comparative NAA was found to be of significant value. Except for a high hafnium blank ($\sim 2 \mu\text{g}$), silica gel grade 923 (100-200 mesh) sold by Aldrich Chemical Company was found to be a highly satisfactory substrate for the preparation of standards. A problem persists in that mercury tends to volatilize if heat is applied to dry samples following solution deposition. A pretreatment of the silica gel

with an anion such as sulfide may solve this problem but has not been studied. In this work, standards were prepared and tagged individually as needed. Future efforts will include attempts to prepare dry SiO_2 based standards in bulk to make the use of such standards more convenient and avoid the problem of finite shelf life of aqueous solutions. The use of a paper packaged plastic drinking straw to replace conventional sample transfer hardware served to further simplify and expedite the preparation of field samples.

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TABLE 1

BLANK ELEMENTAL COMPOSITION

ELEMENT	AVERAGE ug	STANDARD DEVIATION ug	NUMBER OF SAMPLES	AVERAGE DETECTION LIMIT, ug
Al	180	42	7	NA
Mg	35	8	5	45
Mn	0.12	0.02	6	0.1
Ti	27	11	7	NA
As	0.04	0.04	2	0.04
Au	0.01	0.001	1	0.0005
Cd	0.2	0.1	1	0.4
K	6	7	1	33
La	0.003	0.002	2	0.01
Na	13	3	7	NA
Sb	0.02	0.01	6	0.02
Sm	0.001	0.001	5	0.003
W	2.3	0.9	7	NA
Co	0.05	0.04	6	0.03
Cr	1.2	0.3	7	NA
Cs	0.01	0.02	6	0.02
Hf	1.9	0.4	7	NA
Sc	0.001	0.0008	2	0.002
Yb	0.15	0.04	1	0.1

TABLE 2

**ELEMENTS NOT PRESENT
IN BLANK**

ELEMENT	MINIMUM DETECTABLE AMOUNT (ug)
Ba	47
Rb	15
V	0.1
Ga	0.9
U	0.08
Ag	0.06
Ce	0.1
Eu	0.01
Fe	12
Hg	0.1
Lu	0.01
Th	0.03
Se	0.3
Tb	0.01
Zn	2

TABLE 3

COMPARATIVE STANDARD EXAMPLE

ELEMENT	OBSERVED ug	ERROR	PERCENT ERROR	STANDARD AMOUNT ug
Al	4870	25	0.5	4640
Ba	509	7	1.4	494
Mg	473	38	8.1	494
Mn	9.8	0.2	2.2	9.9
Rb	964	33	3.4	988
Ti	1010	16	1.5	988
V	25.0	0.2	1.0	24.7
As	10.2	0.1	1.2	10
Au	0.212	0.002	0.9	0.2
Cd	13.0	0.9	7.3	20
Ga	55	3	5.8	50
K	2030	117	5.8	1000
La	10.10	0.08	0.8	10
Na	101	2	1.9	100
U	20.1	0.3	1.7	20
Sb	5.04	0.04	0.9	5
Sm	0.45	0.02	4.7	1
W	10.0	0.3	3.4	10
Ag	10.2	0.3	3.1	10
Ce	50.4	0.6	1.1	50
Co	9.7	0.1	1.2	10
Cr	49.7	0.8	1.7	50
Cs	10.3	0.1	1.4	10
Eu	9.76	0.08	0.8	10
Fe	1300	68	5.2	1210
Hf	2.06	0.05	2.4	2
Hg	9.5	0.3	3.6	10
Lu	3.07	0.02	0.8	4
Th	3.13	0.06	1.8	3
Sc	0.52	0.01	1.4	0.5
Se	40.4	0.5	1.3	40
Tb	1.03	0.04	4.3	10
Yb	9.7	0.3	3.4	10
Zn	181	3	1.8	200

TABLE 4

NIST SRM 2709, 1633a, and 2711 RESULTS

		NIST VALUE	EXPERIMENTAL CONCENTRATION	PERCENT DIFF
Al (2709)	PPM	75000	72000	4.0
	ERROR	600	5000	
Ba (2709)	PPM	968	800	17.4
	ERROR	40	30	
Mg (2709)	PPM	15100	13000	13.9
	ERROR	500	3000	
Mn (2709)	PPM	538	520	3.3
	ERROR	17	20	
Ti (2709)	PPM	3420	4000	-17.0
	ERROR	240	1000	
V (2709)	PPM	112	120	-7.1
	ERROR	5	10	
As (2709)	PPM	17.7	18	-1.0
	ERROR	0.8	3	
Au (2709)	PPM	~0.3	0.24	20.0
	ERROR		0.09	
K (2709)	PPM	20300	19000	6.4
	ERROR	600	4000	
La (2709)	PPM	~23	19	17.4
	ERROR		2	
Na (2709)	PPM	11600	10100	12.9
	ERROR	300	100	
U (1633a)	PPM	10.2	8	21.6
	ERROR	0.1	1	
Sb (2709)	PPM	7.9	7.7	2.4
	ERROR	0.6	0.2	
Sm (2709)	PPM	~3.8	2.5	34.2
	ERROR		0.3	
W (2711)	PPM	~3	4	-33.3
	ERROR		2	
Ce (2709)	PPM	~42	38	9.5
	ERROR		4	
Co (2709)	PPM	13.4	13	3.0
	ERROR	0.7	2	
Cr (2709)	PPM	130	112	14.1
	ERROR	4	3	
Cs (2709)	PPM	~5.3	5.6	-6.0
	ERROR		0.6	
Eu (2709)	PPM	~0.9	0.8	11.1
	ERROR		0.2	
Fe (2709)	PPM	35000	34000	2.9
	ERROR	1100	2000	
Hf (2709)	PPM	~3.7	3.2	13.5
	ERROR		0.4	
Th (1633a)	PPM	24.7	22.5	8.7
	ERROR	0.3	0.3	
Sc (2709)	PPM	~12	11.7	2.5
	ERROR		0.4	
Se (2709)	PPM	1.57	1.3	14.4
	ERROR	0.08	0.9	
Yb (2711)	PPM	~2.7	2	25.9
	ERROR		1	
Zn (2711)	PPM	~350.4	300	14.3
	ERROR		100	

TABLE 5

COMPARATIVE RESULTS FOR TYPICAL SOIL

ELEMENT	MEAN PPM	STANDARD DEVIATION	MIN PPM	MAX PPM	NUMBER SAMPLES	AVERAGE SENSITIVITY
Al	68000	46000	217	473000	136	NA
Ba	600	1700	31.8	13100	88	5129
Mg	5500	4500	38.2	45700	133	2234
Mn	600	600	0.122	3150	137	NA
Ti	5400	2700	25.7	21600	133	1026
V	80	40	0.06	446	136	NA
As	15	17	3.03	107	134	NA
Au	0.02	0.06	0.001	0.194	10	0.007
Cd	4.0	2.0	1.16	9.95	75	5
Ga	18	8	2.76	50.5	112	16
K	15000	10000	1340	42800	133	189
La	33	12	5.76	63.9	134	NA
Na	690	640	6.88	3190	134	NA
U	4.0	1.6	1.48	17.2	134	NA
Sb	0.8	0.6	0.0805	5.14	128	0.17
Sm	2.4	1.5	0.172	9.65	134	NA
W	8	5	0.698	24.3	99	2
Ag	0.8	0.4	0.286	1.18	4	2
Ce	60	28	13.8	155	136	NA
Co	15	9	2.59	50.4	136	NA
Cr	64	22	20.3	145	136	NA
Cs	4.2	1.6	1.25	8.88	136	NA
Eu	0.7	0.4	0.21	2.42	136	NA
Fe	36000	14000	7920	69700	136	NA
Hf	7	3	1.24	15.1	136	NA
Hg	0.4	0.2	0.221	0.762	4	1
Lu	0.3	0.1	0.0643	0.62	136	NA
Th	11	3	4.28	24	136	NA
Sc	10	5	2.52	22.6	136	NA
Se	0.6	0.5	0.02	2.73	81	2
Tb	0.6	0.4	0.121	3.59	124	0.5
Yb	2.3	1.1	0.0848	4.86	119	2
Zn	160	240	17.3	1740	98	147

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