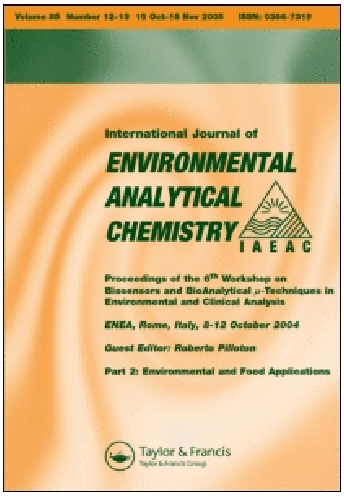

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STUDY OF SEDIMENT SAMPLES USING INSTRUMENTAL PHOTON ACTIVATION MULTI-ELEMENTAL ANALYSIS

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Instrumental Photon Activation Analysis (IPAA) has been used in many fields including environmental geochemistry. In the analysis of soil and sediment samples, the sensitivity of IPAA is comparable to that of standard methods such as atomic absorption spectroscopy. A major advantage of IPAA is that minimal sample processing is required and multi-element analyses can be obtained. In this work, the method of Internal Standard Coupled with Standard Addition Method (ISM-SAM) was applied to IPAA analysis of sediment samples. The equation used in ISM-SAM was derived in detail and the relationship between the elemental mass and the gamma peak counts in the measured spectra was established. It was found that accurate results can be obtained even when the sample and the reference are irradiated at different photon fluxes and measured in different geometries. The ISM-SAM equation was refined to better quantify the relationship between the addition amount and the uncertainty. Applying refined ISM-SAM, a sediment sample from Hudson River was analyzed. The concentrations of Ni, Pb, Zr, Ca, Fe, Mg, Na, Ti, As, Cr, Ce, Co, Rb, and Zn were determined and compared with the results obtained from Atomic Absorption analysis of total acid digests. For elements analyzed by both methods, excellent agreement was found. Meanwhile, the detection limits of photon activation analysis for selected elements were obtained based on the present experimental conditions.

Keywords: Instrumental Photon Activation Analysis; Hudson River Sediment; Internal Standard Method Coupled with Standard Addition Method

INTRODUCTION

Activation analysis is very useful in trace element analysis. In contrast to common chemical analysis methods, activation analysis requires no complicated and time-consuming chemical digestion or separation procedures. Activation analy-

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sis can also determine multiple elements simultaneously. There are basically two activation analysis methods: neutron activation analysis (NAA) and photon activation analysis (PAA). NAA, requiring intensive neutron flux from a nuclear reactor, has been used widely for many applications ranging from biomedical, environmental, geological, industrial, forensic studies [1]. In many situations, however, the use of photon activation analysis (PAA) is more suitable or necessary. As a complementary tool to NAA, PAA has also been successfully used in trace analysis of soil, rock, and sediment [2,3,4], PAA is particularly useful in cases where elements such as Ca, Ni, Ti, Tl and Pb are involved, because these elements are readily analyzed by PAA due to their nuclear characteristics. An advantage of PAA over NAA is that photons can penetrate deeper into a medium so larger samples can be analyzed without destroying the sample.

Other methods, such as Inductively Coupled Plasma Emission Spectrometry (ICPES) and Inductively Coupled Plasma Mass Spectrometry (ICPMS) are also used in elemental analysis. Although these two methods allow for multi-element analysis, they are susceptible to the composition of sample solutions. In many cases, it is required that the major and the minor constituents be removed by chemical procedure to reduce interference effects. In the contrary, Instrumental Photon Activation Analysis (IPAA) is completely an instrumental method, requiring no chemical separation.

In our previous works [5,6], the feasibility and the reliability of Instrumental Photon Activation Analysis based on the facilities at Rensselaer Polytechnic Institute (RPI) have been investigated. The results based on a standard material SRM 1646a sediment obtained from National Institute of Standards and Technology (NIST) indicated that Internal Standard Method (ISM) was reliable and useful.

However, if an unknown sample is to be analyzed, ISM cannot be used directly. This is because ISM requires as an Internal Standard an element with known concentrations in both the sample and the reference. To solve this problem, a new method called Internal Standard Method Coupled with the Standard Addition Method (ISM-SAM) [7,8,9,10] can be used. In others papers, the mathematical equation of the relationship between the elemental mass and the activity of nuclear product after irradiation was deduced. In practice, however, the activities are always obtained through the gamma peak counts in the measured spectra, so it is necessary to directly relate the elemental mass to the gamma peak counts in spectra. M. Yagi et al. [7] pointed out that the advantage of ISM-SAM was that the sample and the reference could be irradiated at different photon flux. Another advantage is that the sample and the reference can be measured in different geometries – an important issue that will be discussed in this paper. From our work it was found that the uncertainty depended on the amount of analyzed element introduced with the Standard Addition, and this relationship is accounted for in our data analysis.

For multi-element determinations, strict use of ISM-SAM, would require that all of the elements of interest be added into the sample, making the analysis quite complicated. We have chosen to simplify multi-element analyses by combining ISM-SAM and ISM. The process consists of two steps. In the first step, several selected elements are added into the sample, and their concentrations are determined by ISM-SAM. In the second step, ISM is applied to determine the concentrations of other elements. A standard reference is irradiated together with the sample, and those elements whose concentrations were obtained by ISM-SAM are used as Internal Standards.

A Hudson River sediment sample was analyzed by the combination of ISM-SAM and ISM in this work. Zr, Ni, and Pb were used for the Standard Additions and the concentrations of Zr, Ni, Pb, Ca, Fe, Mg, Na, Ti, As, Cr, Ce, Co, Rb and Zn were determined. Several aliquots of the same sample had previously been analyzed for Ni, Pb and Zn by flame Atomic Absorption spectroscopy. The objective of this work is to develop the technique of ISM-SAM, for practical application to elemental analysis of sediment samples and to test its reliability based on the facilities at our laboratory.

PRINCIPLE

Theoretically, the mass of an element can be determined by the activity of its photon activation product. However, because the involved nuclear parameters such as photon flux and nuclear reaction cross-sections are either hard to determine or completely unknown, in practical PAA analysis, a comparative method has always been used. For direct comparison, the sample and the reference must receive the same photon flux, which requires the use of a special apparatus. Alternatively, an Internal Standard Method (ISM) [11] can be used. ISM does not require that the photon flux be the same for the sample and the reference, however, there must be at least one element that can be analyzed whose concentrations in both the sample and the reference is known. This element is used as an Internal Standard. For analysis of a complete unknown, three samples are irradiated and counted – the unknown; a duplicate aliquot of the unknown to which known amounts of one or more elements has been added and a standard reference material. Concentrations of the added elements in the unknown are determined by the method of Standard Additions. Any other element can serve as an Internal Standard since the amount in both aliquots of the unknown will be the same. With measured concentrations of added elements in the unknown and certified concentrations of these elements in the standard reference material, the

Internal Standard Method can be applied to determine the concentrations of other elements in the unknown. The overall procedure is called the Internal Standard Method Coupled with Standard Addition Method (ISM-SAM) [7]. Figure 1 shows a diagram of ISM-SAM method. The detailed equation can be derived as follows.

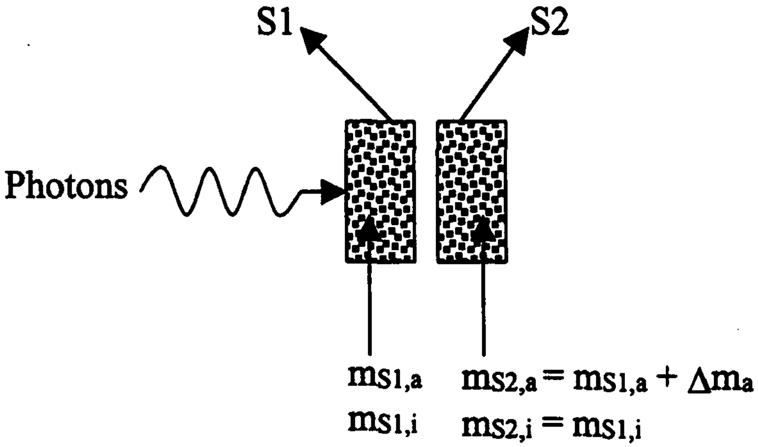

FIGURE 1 The theory of ISM-SAM. S2 is a duplicate of S1; Δm_a of element *a* is added into S2; element *i* is used as Internal Standard

Let *a* represent the element to be analyzed and *i* the element used as the Internal Standard. S1 and S2 are equal-mass aliquots of the sample to be analyzed. The Standard Addition, i.e., the amount of element *a* added into S2, is Δm_a.

After irradiation, the activity of a certain product should be [11]:

$$A = \frac{m \cdot L \cdot h}{A_r} \cdot \varphi \cdot \sigma_{eff} \cdot (1 - e^{-\lambda \cdot T_i}) \qquad (1)$$

Where, A = the activity of the product,

m = the mass of the target element,

L = Avogadro's number,

h = abundance of the target isotope,

A_r = atomic mass of the target isotope,

φ = integral photon flux density,

σ_{eff} = integral effective cross section of the regarded nuclear reaction,

λ = the decay constant of the product,

T_i = the duration of the irradiation.

In practice, the activity is obtained from the net peak area at the gamma energy of the product. The relationship between the activity and the net peak area at the gamma energy is [11]:

$$I = A \cdot \theta \cdot \eta \cdot \frac{e^{-\lambda \cdot T_D}}{\lambda} \cdot (1 - e^{-\lambda \cdot T_C}) \tag{2}$$

Where, I = the net peak area of the regarded gamma energy,

A = the activity of the product,

θ = the branching ratio of the regarded gamma ray,

η = the detection efficiency for the regarded gamma energy,

λ = the decay constant of the product,

T_D = decay period between the end of the irradiation and the beginning of the measurement,

T_C = counting time.

According to equation (1) and (2), for element a and element i in sample S1 and S2, the following equations can be obtained.

$$A_{S1,a} = \frac{m_{S1,a} \cdot L \cdot h_a}{A_{r,a}} \cdot \varphi_{S1} \cdot \sigma_{eff,a} \cdot (1 - e^{-\lambda_a \cdot T_i}) \tag{3}$$

$$I_{S1,a} = A_{S1,a} \cdot \theta_a \cdot \eta_{0,a} \cdot \Omega_{S1} \cdot \frac{e^{-\lambda_a \cdot T_{D,S1}}}{\lambda_a} \cdot (1 - e^{-\lambda_a \cdot T_{C,S1}}) \tag{4}$$

$$A_{S1,i} = \frac{m_{S1,i} \cdot L \cdot h_i}{A_{r,i}} \cdot \varphi_{S1} \cdot \sigma_{eff,i} \cdot (1 - e^{-\lambda_i \cdot T_i}) \tag{5}$$

$$I_{S1,i} = A_{S1,i} \cdot \theta_i \cdot \eta_{0,i} \cdot \Omega_{S1} \cdot \frac{e^{-\lambda_i \cdot T_{D,S1}}}{\lambda_i} \cdot (1 - e^{-\lambda_i \cdot T_{C,S1}}) \tag{6}$$

$$A_{S2,a} = \frac{m_{S2,a} \cdot L \cdot h_a}{A_{r,a}} \cdot \varphi_{S2} \cdot \sigma_{eff,a} \cdot (1 - e^{-\lambda_a \cdot T_i}) \tag{7}$$

$$I_{S2,a} = A_{S2,a} \cdot \theta_a \cdot \eta_{0,a} \cdot \Omega_{S2} \cdot \frac{e^{-\lambda_a \cdot T_{D,S2}}}{\lambda_a} \cdot (1 - e^{-\lambda_a \cdot T_{C,S2}}) \tag{8}$$

$$A_{S2,i} = \frac{m_{S2,i} \cdot L \cdot h_i}{A_{r,i}} \cdot \varphi_{S2} \cdot \sigma_{eff,i} \cdot (1 - e^{-\lambda_i \cdot T_i}) \tag{9}$$

$$I_{S2,i} = A_{S2,i} \cdot \theta_i \cdot \eta_{0,i} \cdot \Omega_{S2} \cdot \frac{e^{-\lambda_i \cdot T_{D,S2}}}{\lambda_i} \cdot (1 - e^{-\lambda_i \cdot T_{C,S2}}) \tag{10}$$

We also have $m_{S1,i}=m_{S2,i}$ and $m_{S2,a}=m_{S1,a}+\Delta m_a$, so the following equation can be obtained

$$\frac{m_{S1,a}+\Delta m_a}{m_{S1,a}}=\frac{I_{S2,a}}{I_{S1,a}}\cdot\frac{I_{S1,i}}{I_{S2,i}}\cdot\frac{e^{-\lambda_a\cdot(T_{D,S1}-T_{D,S2})}}{e^{-\lambda_i\cdot(T_{D,S1}-T_{D,S2})}}\cdot\frac{1-e^{-\lambda_i\cdot T_{C,S2}}}{1-e^{-\lambda_i\cdot T_{C,S1}}}\cdot\frac{1-e^{-\lambda_a\cdot T_{C,S1}}}{1-e^{-\lambda_a\cdot T_{C,S2}}} \tag{11}$$

Let R = the right side of equation (11), so we obtain

$$m_{S1,a}=\frac{\Delta m_a}{R-1} \tag{12}$$

From equation (12), the mass of element a in the sample can be calculated easily, it can be seen that equation (12) only depends on the gamma peak counts $I_{S2,a}$, $I_{S1,a}$, $I_{S1,i}$ and $I_{S2,i}$, those factors of photon flux and gamma measurement efficiency are eliminated, which means the sample and the reference standard can be irradiated at different photon flux and can be measured at different geometries as well.

The relative uncertainty of $\mathrm{m_{S1,a}}$ depends on the uncertainty of R

$$\frac{\sigma_{m_{S1,a}}}{m_{S1,a}}=\frac{1}{1-\frac{1}{R}}\cdot\frac{\sigma_R}{R} \tag{13}$$

R ($=1+\Delta m_a/m_{S1,a}$) is always greater than 1, and its uncertainty depends on the peak counts $I_{S1,a}$, $I_{S2,a}$, $I_{S1,i}$ and $I_{S2,i}$. If R is close to 1, the uncertainty of $m_{S1,a}$will increase significantly. If $R \gg 1$, the uncertainty of $m_{S1,a}$ is close to the uncertainty of R. In practice, larger values of R, and thus lower uncertainties in m_{S1a} can be achieved by increasing the addition amount (Δm_a). If $\Delta m_a$is half of $m_{S1,a}$, the uncertainty of $m_{S1,a}$ will be 3 times the uncertainty of R. If $\Delta m_a$is 5 times $m_{S1,a}$, the uncertainty of $m_{S1,a}$ will be reduced to 1.2 times the uncertainty of R. Based on this analysis, a good choice for the addition amount is a few times the expected value of m_{S1a}.

EXPERIMENTAL

Sample Preparation

The material chosen for analysis was a sediment sample from the Hudson River, SLOSH (Standard Lamont Observatory Sediment from the Hudson) III. SLOSH III is a grab sample consisting of several kilograms of fine-grained surface sediment collected about 40 miles upstream of Manhattan [12]. It consists of 95% silt and clay-sized particles (<63 microns) and 5% sand. It is used primarily as a low-level radionuclide standard, and has also been analyzed several times for trace metals by atomic absorption spectroscopy of total acid digests [13].

In this work, two samples, 3g each, from SLOSH III were prepared. In order to use ISM-SAM, several pure metals (Zr, Ni and Pb) from our lab were added into one of the SLOSH III sample. The purity of Zr, Ni and Pb were examined by photon activation. Each of them was irradiated separately, after irradiation, no impurities were observed in their gamma spectra, which indicated that their purity could be assumed as one hundred percent. The pure metals were in the form of solid pieces, a tiny piece of each metal was cut off and put into the powder of SLOSH III. The addition amount is 0.0024g Zr, 0.0081g Ni and 0.0016g Pb, respectively. To determine the concentrations of other elements using ISM, a standard material, NIST Sediment SRM 1646a was used as a reference. The weight of the SRM 1646a sample was 3.2504 g. The three samples were put into test tubes for irradiation.

Irradiation

Figure 2 shows the arrangement of the irradiation. The samples were located along the axis of the photon flux. The LINAC at Rensselaer Polytechnic Institute was used as irradiation source, the irradiation was performed using bremsstrahlung from a 0.95-cm-thick water cooled Tantalum converter target. The electron energy was 50 MeV, the mean beam current was 80 μA, the irradiation time was 2 hours.

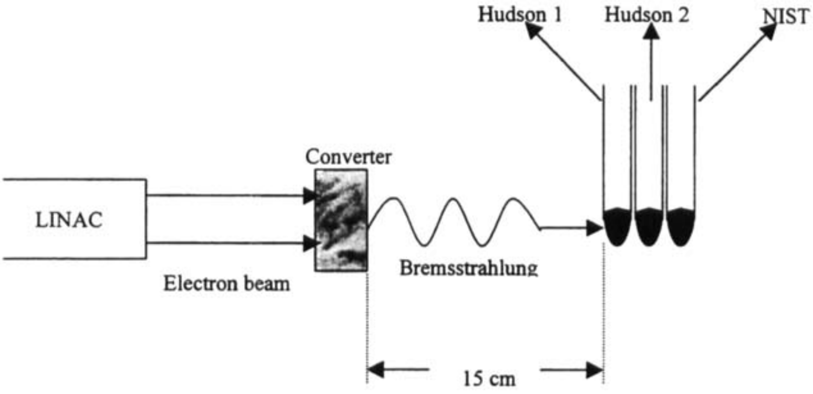

FIGURE 2 The arrangement of irradiation

Gamma Measurement and Spectra Analysis

After irradiation, the samples were allowed to decay for 24 hours, after which they were transferred into clean plastic vials for gamma measurements. The gamma detection system consists of a Canberra HPGe detector, Inspector Module, PC and analysis software Genie 2000 from Canberra Industries. The effective area was 40 cm^2. The samples were located at the surface of the detector.

A series of measurements were made at intervals of 2 or 3 days, the counting time was typically 3 to 4 hours, and the gamma spectra were analyzed automatically with Genie 2000. A measured spectrum of SLOSH III is shown in Figure 3.

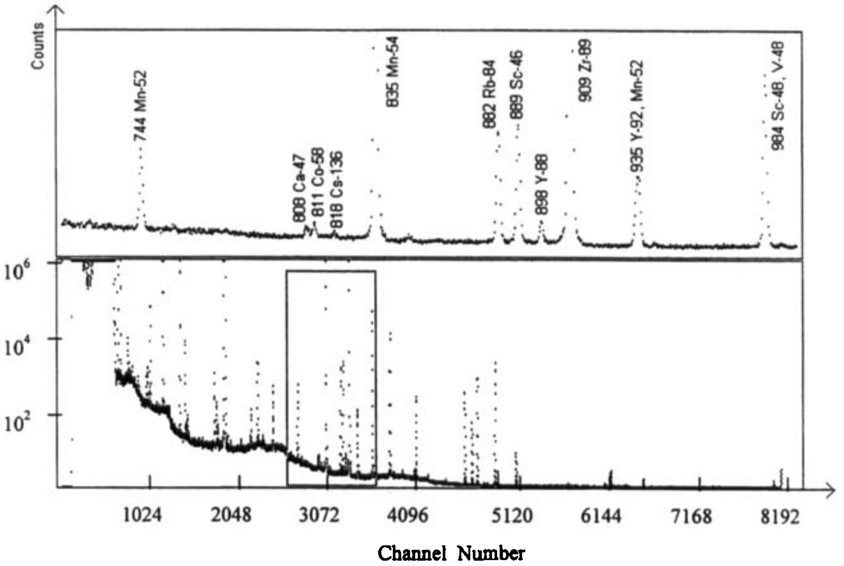

FIGURE 3 Gamma spectrum with high-lighted region expanded in the top panel. Each peak is labeled with the energy in keV and the name of isotope. The spectrum was measured after a 24-hour decay. The counting time was 3 hours

Overall, the entire analysis procedure including sample preparation, irradiation, measurement and analysis took about 2 days. After irradiation, the sample measurement and analysis were conducted automatically with the detection system and spectra analysis software obtained from Canberra. The final results of the elemental concentration could be calculated simply from the counts of the gamma peak in the spectra according to equation 12.

RESULTS AND DISCUSSION

The concentrations of Zr, Ni and Pb were determined using ISM-SAM method. The relevant nuclear reaction and the gamma energies are listed in Table I. The reactions and the gamma energies for Ca, Na and Rb were used as Internal Standards.

TABLE I The nuclear reactions involved

Element[a]	*Reaction*	*Energy (keV)*	*Half-life*
Ni	^{58}Ni(γ,n)^{57}Ni	1378	36h
Pb	^{204}Pb(γ,n)^{203}Pb	279	52.1h
Zr	^{90}Zr(γ,n)^{89}Zr	909	78.4h
Ca	^{44}Ca(γ,p)^{43}K	373	22.2h
Na	^{23}Na(γ,n)^{22}Na	1275	2.6a
Rb	^{85}Rb(γ,n)^{84}Rb	882	34.5d

a. Ca, Na and Rb were used as Internal Standard.

The reactions for Zr and Ni are without any interference. For Pb, ^{204}Hg(γ,n)^{203}Hg also gives off 279 keV gamma rays, but the half-life (46.6d) is much longer than that of ^{203}Pb (52.1h). When sample was been measured after a one-month decay, the 279 keV energy was not observed, indicating that the original 279 keV gamma peak originated solely from ^{203}Pb. As for the reactions used as Internal Standards, ^{44}Ca(γ,p)^{43}K is without any interference. For Na, although ^{24}Mg(γ,np)^{22}Na and ^{27}Al(γ,αn)^{22}Na produce ^{22}Na, their contribution is negligible compared to ^{23}Na(γ,n)^{22}Na[11]. For Rb, ^{86}Sr(γ,np)^{84}Rb also produce ^{84}Rb, but also in negligible amounts.

The concentrations of Zr, Ni and Pb were calculated and the results are listed in Table II. The errors are 1σ standard deviation based on the gamma counting statistics. The results for Ca and Rb as Internal Standard are in excellent agreement. The results for Na as internal standard are lower than those with Ca and Rb consistently, the ratios of concentrations between the data with Na and the data with Ca or Rb are equal. This fact is in accordance with equation (11), because in the calculations of concentration, the item $I_{S1,i}/I_{S2,i}$ with Na is lower than that with Ca and Rb. And because the peak counts of ^{22}Na are lower, the errors with Na are higher than those with Ca and Rb. Overall, the values obtained using the different Internal Standards are in good agreement with each other. The results from different Internal Standards were averaged with weight according to with their errors.

TABLE II The concentrations of Zr, Ni and Pb using ISM-SAM

Internal Standard	*Concentration (μg/g)*		
	Zr	*Ni*	*Pb*
Ca	255.6(1.6%)	54.3(1.8%)	168.2(1.9%)
Na	248.6(7.3%)	53.1(5.9%)	164.5(6.0%)
Rb	255.7(4.4%)	54.3(3.7%)	168.3(3.8%)
Average	255.3(1.5%)	54.2(1.6%)	167.9(1.6%)

Once the concentrations of Zr, Ni and Pb were determined, it became possible to measure the concentrations of other elements in Hudson River Sediment using one of the three elements as the Internal Standard and NIST SRM 1646a as the reference. Because of better statistical characteristics of the gamma energy peak, Zr was chosen as Internal Standard in this work. The concentration of Zr in SRM 1646a was not given by NIST, but it had been determined in our previous work [6], the value is 410.4 μg/g.

The concentrations of Ca, Fe, Mg, Na, Ti, As, Cr, Ce, Co, Rb and Zn in SLOSH III were determined and the results are listed in Table III along with their uncertainties. The uncertainties are based on the gamma counting statistics. All of the used reactions and the selected gamma rays are without significant interference [11].

TABLE III The elemental concentrations in Hudson River Sediment

Element	*Reaction*	*Gamma energy (keV)*	*Concentration (μg/g)*
Ca	$^{44}Ca(\gamma,p)^{43}K$	373	14654.0(1.5%)
Fe	$^{54}Fe(\gamma,np)^{52}Mn$	744	52776.2(1.5%)
Mg	$^{25}Mg(\gamma,p)^{24}Na$	1369	12326.0(1.5%)
Na	$^{23}Na(\gamma,n)^{22}Na$	1275	12790.8(1.5%)
Ti	$^{49}Ti(\gamma,p)^{48}Sc$	175	6401.4(1.5%)
As	$^{75}As(\gamma,n)^{74}As$	596	18.6(6.9%)
Cr	$^{52}Cr(\gamma,n)^{51}Cr$	320	146.9(1.5%)
Ce	$^{140}Ce(\gamma,n)^{139}Ce$	166	121.7(1.5%)
Co	$^{59}Co(\gamma,n)^{58}Co$	811	35.0(10.3%)
Rb	$^{85}Rb(\gamma,n)^{84}Rb$	882	177.0(1.5%)
Zn	$^{66}Zn(\gamma,n)^{65}Zn$	1116	321.6(12.2%)

The concentrations of Ni, Pb and Zn in SLOSH III had been previously determined by total acid digestion with analysis by flame atomic absorption spectroscopy. The values obtained are listed in Table IV along with the results of this work. The error of Zn from this work is high (12.2%), the reason is that the concentration of Zn in SRM 1646a which was used as Standard Reference is low (48.9 μg/g), so the counting rate of the relevant gamma energy is low, which means higher statistical error. Better result for Zn can be expected if using Addition Method or using other Standard Reference Material. The differences between the data from this work and those from atomic absorption are 9.7% for Ni, 4.7% for Pb and 4.0% for Zn, respectively. Because this work is a primary research focused on the examination of the reliability of ISM-SAM in environmental sample analysis, the experiment was designed as simply as possible. First, the added pure metals were in the form of tiny solid pieces and not well mixed with the powder of SLOSH III, this may cause some errors due to the position change of those metals in the sample. Second, the selected standard reference SRM 1646a was not very suitable for the determination of several elements such as Zn due to their low concentrations. If the added elements are well mixed with the sample and more suitable standard reference is used, better results can be obtained. Even under the present experimental conditions, the results in this work are still in agreement with those from atomic absorption within a certain range of error. This indicates that IPAA has significant potential as a technique for multi-element analysis of sediment and soil samples. Most attractive is the fact that the IPAA method avoids the complicated and time-consuming acid digestion steps common to atomic absorption and inductively coupled plasma techniques.

TABLE IV Comparison of the IPAA results for SLOSII III with those from Atomic Absorption

Element	*Concentration (μg/g)*	
	This work[a]	*Atomic absorption*[b]
Ni	54.2 (1.6%)	60.0 (2.3%)
Pb	167.9 (1.6%)	160.3 (5.7%)
Zn	321.6 (12.2%)	309.3 (4.6%)

a. The reported e are 1σ standard deviation based on the gamma counting statistics.

b. The reported values for Zn and Pb are the means of analyses of 9 aliquots of SLOSH III 1σ standard deviation. The data for Ni is based on analyses of 3 aliquots of this sample.

Finally, in order to give an idea how sensitive PAA can reach, the detection limits for Ca, Fe, Mg, Na, Ti, Ni, Pb, Zr, As, Cr, Ce, Co, Rb and Zn were calculated according to the following equation:

$$\text{Detection-limit} = C \cdot \frac{2\sqrt{B}}{A} \qquad (14)$$

Where, A is the height of the counts of the gamma peak, B is the background counts, C is the concentration of the regarded element.

The detection limits are listed in Table V, the related nuclear reactions and gamma rays can be found in Table I and Table III.

TABLE V The detection limits of PAA for selected elements

Element	*Detection limit (μg/g)*
Ca	238
Fe	1541
Mg	45
Na	86
Ti	289
Ni	1.4
Pb	5.8
Zr	0.5
As	1.2
Cr	3.3
Ce	2.1
Co	3.6
Rb	2.2
Zn	37

CONCLUSION

The complete formula for Internal Standard Method Coupled with Standard Addition method was derived. Another advantage of this method was found, namely that the sample and the reference can be measured at different geometries and irradiated at different photon fluxes. This makes ISM-SAM much easier to use. The relationship between the uncertainty and the addition amount was specified. Applying ISM-SAM, the elemental concentrations in Hudson River sediment were determined. The results indicate that ISM-SAM is reliable and effective and that Photon Activation Analysis is a useful technique for multi-element analysis of sediment and soil samples.

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