



Photon activation analysis: a proof of principle using a NIST sediment standard and an electron accelerator at Rensselaer Polytechnic Institute

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Abstract

Photon activation analysis was performed using a standard sediment SRM 1646a and the Bremsstrahlung X-ray from a LINAC at RPI. The selected electron energy was 50 MeV and the mean beam current was 80 μA . Using Internal Standard Method, the concentrations of Ni and Pb has been determined, the results agree well with the values given by National Institute of Standards and Technology (NIST). However, a large amount of Zr in SRM 1646a was discovered which was not in the NIST certificate. The concentration of Zr was also determined. Finally, the PAA sensitivities for Ca, Ti, As, Pb, Ce, Ni, Rb and Zr based on the present experimental conditions were presented. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Photon activation analysis; Internal Standard Method; Sediment sample

1. Introduction

Activation analysis is a very useful tool in trace element analysis. Compared with the chemical analysis method, activation analysis is non-destructive and requires no complicated and time-consuming chemical separation procedure. Activation analysis can also determine multiple elements simultaneously. There are basically two activation analysis methods, namely Neutron Activation Analysis (NAA) and Photon Activation Analysis (PAA). NAA which requires intense neutron flux from a nuclear reactor has been used widely for many applications, ranging from biomedical, environmental, geological, industrial studies and so

on. On the other hand, there are many situations that the use of PAA is more suitable or necessary. As a complementary tool to NAA, PAA has been successfully demonstrated in trace analysis of soil (Fusban et al., 1981; Landsberger and Davidson, 1985), rock (Kato et al., 1973), sediment (Berthelot et al., 1980) samples and so on. PAA is particularly useful in cases where elements such as Ca, Ni, Ti, Tl and Pb are involved, because these elements can be analyzed by PAA effectively. Another advantage of PAA over NAA is that photons can penetrate deeper into a medium so large sized samples can be irradiated.

The general procedure of PAA consists of two steps, first the samples are irradiated by photons which are always produced from an electron accelerator; second the irradiated sample will be measured with Gamma spectrometer, and by analyz-

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ing the gamma spectra, the quantities of the elements in the samples can be determined.

Because some involved nuclear parameters such as photon flux and nuclear reaction cross sections are hard to determine or completely unknown, so the mass of the element is not obtained directly from the activity of the product. Instead, a reference standard is always irradiated with the unknown sample simultaneously, and the content of a certain element in the unknown sample can be obtained by comparing the activities of the same product both in the unknown sample and the reference standard, this way the factors such as photon flux and reaction cross section are not needed to be considered. But in this comparative method, it is required that the unknown sample and the reference standard must receive the same photon flux during irradiation, actually some kind of special apparatus were designed to achieve this aim (Berthelot et al., 1980; Landsberger and Davidson, 1985).

An alternative method called Internal Standard Method (ISM) has been proposed by others (Yagi and Masumoto, 1984, 1987), ISM does not require that the reference standard and the unknown sample must receive the same photon flux, even more, they can be irradiated separately at the same energy. But ISM requires an element whose contents are known in both of the unknown sample and the reference standard, so this element can be used as an internal standard. If such an element does not exist, one can add an element into both the unknown sample and reference standard, and use this element as internal standard, of course one should choose the suitable internal standard carefully.

The LINAC laboratory of Rensselaer Polytechnic Institute (RPI) is equipped with a powerful electron accelerator whose electron energy can reach 60 MeV, this accelerator is very suitable to be used as a photon source for PAA, also a set of high quality gamma measurement system with a HPGe is available for sample analysis. These facilities make it possible to conduct PAA research at our laboratory. In this work, the main purpose is to examine the analysis capability of PAA based on our facilities. A standard material SRM 1646a Sediment obtained from National Institute of Standards and Technology (NIST) was analyzed, ISM was used in our research, because it does not need to maintain the same photon flux for all unknown samples and the reference standard. Using Iron as internal standard, the concentrations of Pb and Ni were obtained, the results were in good agreement with the data given by NIST. Meanwhile, during the analysis, it was found there existed Zirconium in SRM 1646a, but NIST does not give any information about the concentration of this element, in our work, the content of Zr has also been determined. Finally, the

analysis sensitivities for Ca, Ti, As, Pb, Ce, Ni, Rb and Zr were obtained.

2. Principle

After irradiation, the activity of a certain product should be (Segebade et al., 1988):

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

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 of a certain gamma energy, the relationship between the activity and the net peak area of the gamma energy is (Segebade et al., 1988):

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

where: I = the net peak area of the regarded gamma energy, A = the activity of the product, θ = the branch ratio of the regarded gamma energy, 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.

Theoretically, m can be obtained by Eqs. (1) and (2), but because those factors such as ϕ and σ_{eff} are either hard to determine or completely unknown, generally Eqs. (1) and (2) are not used directly in practice. Instead, a reference standard material is irradiated together with the unknown sample.

After irradiation, the activities of a certain product in the unknown sample and the reference standard should be:

$$A_s = \frac{m_s \cdot L \cdot h_s}{A_r} \cdot \varphi \cdot \sigma_{\text{eff},s} \cdot (1 - e^{-\lambda T_{i,s}}) \quad (3)$$

$$I_s = A_s \cdot \theta \cdot \eta_s \cdot \frac{e^{-\lambda T_{D,s}}}{\lambda} \cdot (1 - e^{-\lambda T_{C,s}}) \quad (4)$$

$$A_R = \frac{m_R \cdot L \cdot h_R}{A_r} \cdot \varphi_R \cdot \sigma_{\text{eff},R} \cdot (1 - e^{-\lambda T_{i,R}}) \quad (5)$$

$$I_R = A_R \cdot \theta \cdot \eta_R \cdot \frac{e^{-\lambda T_{D,R}}}{\lambda} \cdot (1 - e^{-\lambda T_{C,R}}) \quad (6)$$

Because the sample and the reference are irradiated at the same energy simultaneously, we have $\sigma_{\text{eff}, s} = \sigma_{\text{eff}, R}$ and $T_{i, s} = T_{i, R}$. From Eqs. (3), (4), (5) and (6), the following can be obtained:

$$\frac{m_S}{m_R} = \frac{I_s}{I_R} \cdot \frac{e^{-\lambda \cdot T_{D, R}}}{e^{-\lambda \cdot T_{D, S}}} \cdot \frac{1 - e^{-\lambda \cdot T_{C, R}}}{1 - e^{-\lambda \cdot T_{C, S}}} \cdot \frac{\varphi_R}{\varphi_S} \cdot \frac{\eta_R}{\eta_S} \quad (7)$$

From Eq. (7), it can be seen that if the photon flux and the gamma efficiency can remain as constant for the sample and the reference, namely $\varphi_R = \varphi_S$ and $\eta_R = \eta_S$, m_S can be easily obtained. As mentioned above, in order to keep the photon flux a constant, some kind of special apparatus is required.

Another way to solve the problem of the difference of the photon flux is a method called Internal Standard Method (ISM). In this method, assuming that there is an element whose contents are known in both the sample and the reference, this element can be used as an internal standard. In the following deduction, a stands for the element to be analyzed, i stands for the element to be used as internal standard. According to Eq. (7), we have:

$$\frac{m_{S, a}}{m_{R, a}} = \frac{I_{S, a}}{I_{R, a}} \cdot \frac{e^{-\lambda_a \cdot T_{D, R}}}{e^{-\lambda_a \cdot T_{D, S}}} \cdot \frac{1 - e^{-\lambda_a \cdot T_{C, R}}}{1 - e^{-\lambda_a \cdot T_{C, S}}} \cdot \frac{\varphi_I}{\varphi_S} \cdot \frac{\eta_{R, a}}{\eta_{S, a}} \quad (8)$$

$$\frac{m_{S, i}}{m_{R, i}} = \frac{I_{S, i}}{I_{R, i}} \cdot \frac{e^{-\lambda_i \cdot T_{D, R}}}{e^{-\lambda_i \cdot T_{D, S}}} \cdot \frac{1 - e^{-\lambda_i \cdot T_{C, R}}}{1 - e^{-\lambda_i \cdot T_{C, S}}} \cdot \frac{\varphi_R}{\varphi_S} \cdot \frac{\eta_{R, i}}{\eta_{S, i}} \quad (9)$$

Meanwhile we have:

$$\frac{\eta_{R, a}}{\eta_{S, a}} = \frac{\eta_{R, i}}{\eta_{S, i}} = \frac{\Omega_R}{\Omega_S} \quad (10)$$

Where, Ω_R and Ω_S are the measurement solid angles for the reference standard and the sample respectively.

From Eqs. (8), (9) and (10), we obtain:

$$m_{S, a} = \frac{m_{R, a} m_{S, i}}{m_{R, i}} \cdot \frac{I_{S, a}}{I_{R, a}} \cdot \frac{I_{R, i}}{I_{S, i}} \cdot \frac{e^{-\lambda_a \cdot T_{D, R}}}{e^{-\lambda_a \cdot T_{D, S}}} \cdot \frac{e^{-\lambda_i \cdot T_{D, S}}}{e^{-\lambda_i \cdot T_{D, R}}} \times \frac{1 - e^{-\lambda_a \cdot T_{C, R}}}{1 - e^{-\lambda_a \cdot T_{C, S}}} \cdot \frac{1 - e^{-\lambda_i \cdot T_{C, S}}}{1 - e^{-\lambda_i \cdot T_{C, R}}} \quad (11)$$

Eq. (11) is the formula which is used in ISM, it can be seen that due to the introduction of the internal standard, not only the factors φ_R and φ_S are dropped out, but also the gamma efficiency factors are dropped out. This makes it possible that the sample and the reference can be irradiated at the different photon flux and also they can be measured at different geometry. These two facts make ISM very easy to handle, one does not need to pay much attention to arrange the sample and the reference carefully either in the irradiation nor in the gamma measurement.

3. Experiment

3.1. Sample preparation

A standard material SRM 1646a Sediment obtained from NIST was used as sample, two independent samples were weighed and put into glass test tubes, they were named Sample 1 and Sample 2 respectively, the weights were 1.9805 g for Sample 1 and 2.0237 g for Sample 2.

Because photons have stronger penetration capability, it is not required that the matrix of the reference material be similar to the unknown sample. In our work, pure metals were adopted in the preparation of the reference standard, 0.0830 g of Fe, 0.3097 g of Ni, 0.5852 g of Pb and 0.0310 g of Zr were wrapped together with aluminum foil, this sample will be used as the reference standard.

3.2. Irradiation

Fig. 1 shows the arrangement of the samples and the reference standard during irradiation, they were located along the axis of the photon flux. The LINAC machine 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 and the mean beam current was 80 μA , the irradiation time was 2 h.

3.3. Measurement and spectra analysis

After irradiation, the samples were allowed to decay for 24 h, after which Sample 1 and Sample 2 were transferred into plastic vials, and the pure metal reference sample was unwrapped and then re-wrapped with fresh aluminum foil.

The gamma detection system consists of a Canberra HPGc detector, Inspector Module, PC and analysis software Genie 2000 (InSpector, Canberra Industries,

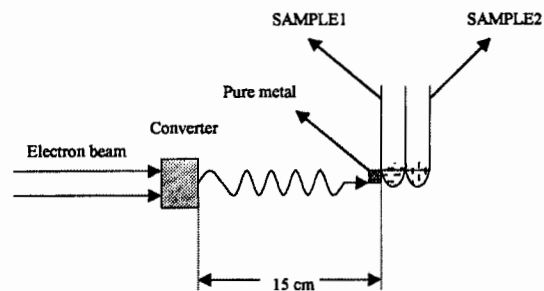


Fig. 1. The arrangement of the samples and the reference standard during irradiation.

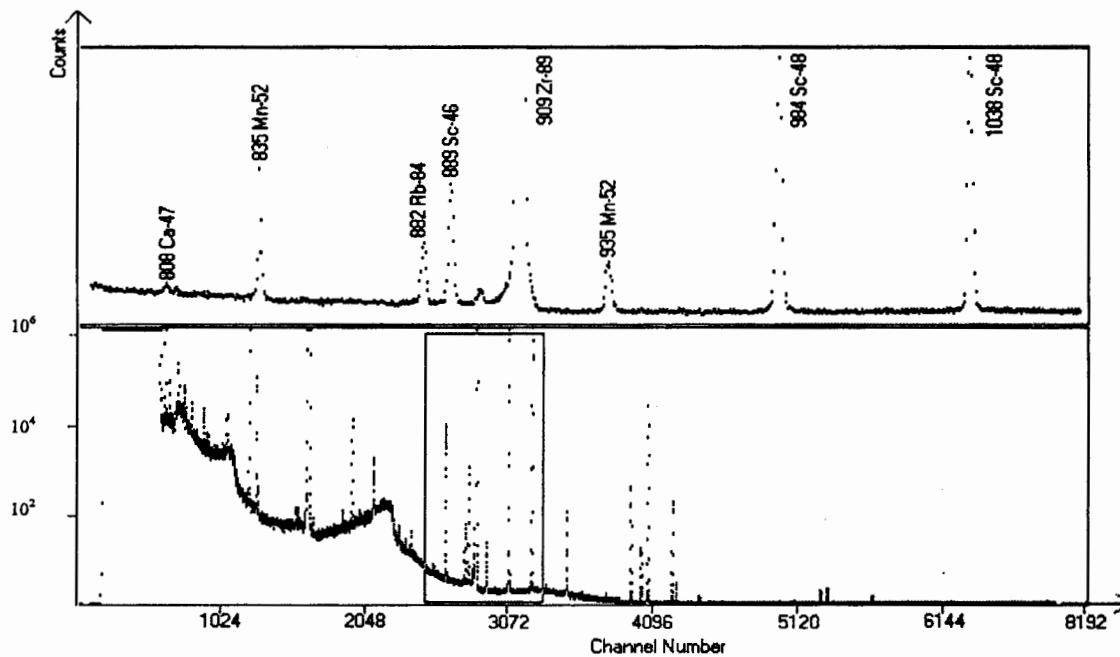


Fig. 2. Gamma spectrum with high-lightened region expanded in the top panel. Each peak is labeled with the energy in keV and the name of isotope. The counting time was 5 h.

Meriden, CT). The effective volume of the detector is 40 cm^3 . The NIST samples were put at the surface of the detector, the reference was put at the distance of 2.5 cm from the detector.

A series of measurements were made at intervals of 2 or 3 days, the counting time was about 3–4 h, the gamma spectra were analyzed automatically with Genie 2000.

A measured spectrum of NIST sample is shown in Fig. 2, it consists of nearly 80 gamma peaks.

4. Results and discussion

4.1. The nuclear reactions used for PAA

In PAA, the selection of activation products is very

Table 1
Nuclear reactions used in PAA

Element	Reaction	Energy (keV)	Half-life
Fe	$^{54}\text{Fe}(\gamma, np)^{52}\text{Mn}$	744	5.7 days
Ni	$^{58}\text{Ni}(\gamma, n)^{57}\text{Ni}$	1378	36 h
Pb	$^{204}\text{Pb}(\gamma, n)^{203}\text{Pb}$	279	52.1 h
Zr	$^{90}\text{Zr}(\gamma, n)^{89}\text{Zr}$	909	78.4 h

important. It is required that the products have suitable gamma energies and the half-lives. The most important is that the selected gamma energies be interference free, which means these gamma energies can not be overlapped by other energies, and the selected product should not be produced by other elements. Table 1 gives the reactions used in this work.

The reactions for Fe, Ni and Zr are without any interference, as for Pb, $^{204}\text{Hg}(\gamma, n)^{203}\text{Hg}$ also gives off 279 keV gamma rays, but the half-life (46.6 days) is much longer than ^{203}Pb , the sample has been measured after a 1-month decay, the 279 keV energy was not observed, which shows that the 279 keV gamma peak is solely originated from ^{203}Pb .

Table 2
The concentrations of Ni, Pb and Zr

Element	Concentration			NIST data
	Sample 1	Sample 2	Average	
Ni	22.9 ± 1.6	22.7 ± 1.2	22.8 ± 1.0	23^a
Pb	15.0 ± 2.2	13.4 ± 1.7	14.0 ± 1.4	11.7 ± 1.2
Zr	412.8 ± 28.4	417.0 ± 22.7	415.4 ± 17.7	b

^a NIST doesn't give the uncertainty.

^b NIST doesn't give the concentration of zirconium.

Table 3
The PAA sensitivities for selected elements

Element	Reaction	γ -Energy (keV)	Sensitivity (μg)	
			Present work	Segebade et al. (1988)
Ca	$^{44}\text{Ca}(\gamma, p)^{43}\text{K}$	373	26.9	8
Ti	$^{49}\text{Ti}(\gamma, p)^{48}\text{Sc}$	984	21.5	18
As	$^{75}\text{As}(\gamma, n)^{74}\text{As}$	596	0.9	0.5
Pb	$^{204}\text{Pb}(\gamma, n)^{203}\text{Pb}$	279	3.9	1
Ce	$^{140}\text{Ce}(\gamma, n)^{139}\text{Ce}$	166	1.1	0.6
Ni	$^{58}\text{Ni}(\gamma, n)^{57}\text{Ni}$	1378	1.6	0.9
Rb	$^{85}\text{Rb}(\gamma, n)^{84}\text{Rb}$	882	3.5	2
Zr	$^{90}\text{Zr}(\gamma, n)^{89}\text{Zr}$	909	0.7	0.3

4.2. The concentrations of Ni, Pb and Zr in SRM 1646a

In the measured spectra, the gamma energies of 909, 1621, 1657, 1713 and 1744 keV were observed, they were originated from $^{90}\text{Zr}(\gamma, n)^{89}\text{Zr}$, which shows that there exists Zr in SRM 1646a, but NIST does not give the concentration of Zr.

ISM was used to determine the concentrations of Ni, Pb and Zr, Fe was used as internal standard element, the results are listed in Table 2 along with the data given by NIST.

From Table 2, it can be seen that the results from Sample 1 and Sample 2 agree with each other and they are all in good agreement with the values given by NIST, moreover, we obtained the concentration of Zr which was not included with NIST information.

4.3. The analysis sensitivities

Basically, sensitivities in PAA strongly depend on a large variety of experimental parameters such as the electron energy, beam current, irradiation time, gamma detection efficiency, etc. and therefore the sensitivities are barely reproducible when using different devices. In spite of this, it still makes some sense to give an idea of the order of magnitude of the sensitivity achievable with PAA. In this work, the concept of sensitivity defined by Segebade et al. (1988) was adopted. The

sensitivity is defined as the amount of the element that can cause one thousand counts during counting time of 12 h after a decay period of 24 h. Therefore, the sensitivity can be calculated using following equation:

$$m_s = \frac{\lambda \cdot 1000}{1 - e^{-\lambda \cdot 12}} \cdot e^{\lambda \cdot 24} \times m_x \quad (12)$$

$$\frac{\lambda \cdot c_m}{1 - e^{-\lambda \cdot t_m}} \cdot e^{\lambda \cdot t_d}$$

where: m_s = the sensitivity, m_x = the mass of the regarded element in the sample, c_m = real counts, t_m = real counting time, t_d = real decay time, λ = decay constant of the product.

The change of activity during counting time has been taken into consideration in Eq. (12).

Because the elemental concentrations of SRM 1646a have been given by NIST, the amount of the elements in the samples used in this work are known. Using these data and Eq. (12), the sensitivities for Ca, Ti, As, Pb, Ce, Ni and Rb has been obtained, the sensitivity of Zr is also calculated, but because NIST does not provide the concentration of Zr, the sensitivity is based on the concentration data obtained by our research. All of the results are listed in Table 3 along with the results given by Segebade et al. (1988).

As mentioned above, the sensitivity depends strongly on the experimental conditions, the relevant par-

Table 4
Irradiation and measurement conditions

Operating parameters	Present work	Segebade et al. (1988)
Electron energy	50 MeV	30 MeV
Beam current	80 μA	150 μA
Duration time	2 h	0.5–2 h
Distance between sample and the Bremsstrahlung target	15 cm	8 cm
γ -detector effective area	40 cm^2	50 cm^2
The distance between the source and the γ -detector	At the surface of the detector	At the surface of the detector

ameters of ours and those of Segebade et al. (1988) are shown in Table 4.

From Table 4 it can be seen that in our research, the beam current is nearly half of Segebade's (Segebade et al., 1988), the distance between the sample and the converter target is twice as their work, and their gamma detector has a larger effective area than ours. All these factors contribute to the better sensitivities obtained by Segebade. If we change the experiment parameters, better sensitivities can be expected. Generally the sensitivity under our experimental conditions are roughly in the same order of magnitude as Segebade's, and these sensitivities are sufficient for trace elemental analysis.

5. Conclusion

The photon activation analysis has been successfully conducted at LINAC laboratory at RPI. A standard material SRM 1646a was analyzed using Internal Standard Method. The obtained concentrations of Ni and Pb agree well with the data given by NIST, and the concentration of Zr was also determined, Zr concentration was not included with information obtained from NIST on SRM 1646a. The analysis sensitivities for Ca, Ti, As, Pb, Ce, Ni, Rb and Zr have been pre-

sented. All of the results show that it is possible to achieve reliable results with the PAA equipment at LINAC labs.

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