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Measurement and analysis of photonuclear reactions on thick target samples of biological importance

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A novel method for quantification of trace elements in herbal samples using photon activation analysis is reported. Seven trace elements have been detected and their concentrations have been estimated from residue yields after the photo-nuclear reaction. This method can complement the conventional neutron activation analysis for trace elemental detection**.** The data is useful for setting referral standards for quality assurance of herbs and herbal formulations commercially available for therapeutic purposes. This is a relatively simple, novel and sensitive method for trace elemental analysis which can be scaled to suit industrial and statutory requirements of standardization and quality control.

Keywords: Gamma activation, Medical LINAC, Bremsstrahlung, Herbal medicines

1 Introduction

Nuclear reaction data has fundamental applications in various branches of science and technology. Nuclear physics, reactor physics, astrophysics, and radiation therapy are fundamental areas of application of nuclear data. The analytical power of nuclear reaction data has been used as an efficient tool for the characterization of materials as well as for quality assurance. Nuclear activation methods like Neutron Activation Analysis (NAA), Prompt Gamma Neutron Activation Analysis (PGNAA) and Photon Activation Analysis (PAA) forms the best analytical tools for the characterization of materials and has applications in physical chemical and biological sciences, which enables simultaneous detection of many elements with high sensitivity and least chemical procedures.

High energy electron and photon beams have been widely used for radiation therapy and material modification. A large number of installations with electron beams of energy ranging from 4 to 20 MeV have been commissioned in various parts of the country, primarily for treatment purposes. These electron beams produce Bremsstrahlung photons which are also used for treatment purposes. Moreover, these high energy photons induce photo-nuclear reactions. (γ, γ'), (γ, n), (γ, p) and (γ, α) are found to be the prominent nuclear reactions possible in this energy range. This has potential applications in radiation dosimetry as well as material analysis.

Photon activation analysis has been considered as a sensitive method used for elemental analysis of a wide variety of samples like ancient artifacts, ores, biological materials like tooth, bones, etc[1-5]. Elements such as Be, C, N, O, F, Si, P, Ni, Tl, Pb and Bi which are difficult to detect by NAA can be quantified with high detection power in PAA [6]. Excessive matrix activity, inhomogeneous activation due to large absorption cross-sections, etc. are significantly reduced in PAA[6]. Moreover, the resonance behaviour of the neutron spectrum, especially at the epithermal region introduces neutron self-shielding effects which increase the uncertainty in the obtained results[7]. Another advantage of PAA over NAA is the penetration power. Photons penetrate deeper into the medium and hence larger samples can be analysed without destruction of the sample[8]. Moreover, the limited availability of NAA facilities, as it requires reactor set up in order to impart high flux of neutrons of the order of 10^{13} $ncm^{-2}s^{-1}$ poses a severe constraint for NAA. Considering the above aspects, a method of trace elemental analysis of multi-elemental samples using medical LINAC (Linear Accelerator) is a promising technique. Canel *et al.* (2016) and Chaoa *et al.* (2009) and Stamatelatos (2016) *et al.* reported the application of medical LINAC for the analysis of different sample types[9-11]. The growing demand for medical LINACs for treatment purposes provides

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better accessibility to photon source for photon activation analysis.

Herbal medicines are widely accepted as an alternative way of treatment of diseases. India is a well-established hub for herbal treatment and the industry is expanding rapidly. The standardization and quality authentication of these medicines and their ingredients is a tough task in the pharmaceutical industry. The development of a scientific method for quality assurance is a child yet to be born. The sensitivity of an analytical method matters mostly when the determination of elements of microgram order is required for a sample, in a matrix of major elements of the order of many grams, within acceptable limits of uncertainty. The present work reports the trace elemental analysis of herbal sample-Phyllanthus emblica (English name-Emblic myrobalan, Local name-Amla) using the photon activation method. P. emblica is a good source of dietary vitamin C, amino acids and minerals. The anti-oxidant, anti-inflammatory and anti-diarrheal properties of the fruits of the herb are well reported[12-15]. Here, high energy bremsstrahlung photons with end point energy of 20 MeV are made to interact with a thick target sample of P. emblica and the resulting gamma lines are identified. The characteristic gamma lines produced by the (γ, n) and (γ, γ') reactions are investigated. ^{115}In (γ, γ')^{115}In reaction has been used for monitoring the photon flux. The contribution of trace elements along with some minor elements is identified and quantified. The data is expected to complement other techniques used for trace elemental detection.

2 Theory

In PAA, the nuclides present in the target sample are made radioactive through exposure to high energy photons. The nuclei undergo radiative decay and emit characteristic gamma lines. The elemental concentration is calculated from the reaction yield corresponding to the respective energies using the formula:

$$C_m = \frac{mN_A \varepsilon I A_0}{A} \frac{(1-e^{-\lambda t_1})(1-e^{-\lambda t_2})(e^{-\lambda t_3})}{\lambda} \int_{E_{th}}^{E_{max}} \sigma(E)\phi(E)dE$$

where, m is mass of the sample, N_A is the Avogadro number, ε is the energy-dependent efficiency of the detector, I is the branching ratio, A_b is the abundance of the isotope, A is the natural atomic number of the target isotope, σ is the spectrum averaged cross-section, ϕ is the normalized flux, λ is the decay constant for the particular isotope, t_1 is the irradiation time, t_2 is the counting time, and t_3 is the cooling time in seconds. For the monitor In, the number of particles per unit area undergoing exposure is calculated from the weight of the sample. The ratio method is used to find the number of particles present in the sample belonging to each element.

3 Experimental Details

Dried fruits of the herb P. emblica were collected from the authentic sources and were identified and certified from Centre for Medicinal Plant Research, Kottakkal Arya Vaidyasala, Kottakkal, Kerala. The samples were washed in double-distilled water and dried in vacuum at 110 ºC. The dried samples were ground after removal of seeds in stainless steel grinder followed by sieving with sieve no: 80 to ensure homogeneity. About 15 g of the sample was taken and subsequently pressed with a pressure of 9 Ton to get a compact sample for irradiation. Simultaneous irradiation of ^{115}In was done by keeping the foil on the top of the sample pellet, for the flux normalization via ^{115}In (γ, γ') ^{115}In reaction.

A 20 MeV electron beam of ~35 μA, produced using Varian CLINAC-iX, medical linear accelerator (LINAC), falling on a 1mm Pb target produces the high-intensity bremsstrahlung with end point energy of 20 MeV. The sample was attached to the bottom of the Pb bremsstrahlung target, along with the flux monitor to get the maximum bremsstrahlung flux. Irradiation was done for 20 minutes with this configuration for achieving a measurable level of induced activity. Gamma spectrum from the irradiated samples was acquired using Kromeck-CZT (Cadmium Zinc Telluride semiconductor detector) gamma spectrometer, having a crystal size of 1cm×1cm×1cm and resolution of 32 keV at 661 keV. Counting was performed for different intervals after sufficient cooling, to get good statistics for both short and long-lived nuclides. Separate counting of the monitor was done, to minimize the random coincidence effects.

The energy and efficiency calibration of the CZT detector was done using standard calibration sources of known activity viz. ^{22}Na, ^{137}Cs, ^{133}Ba, and ^{60}Co. The energy-dependent efficiency was calculated and the plot is shown in Fig. 1. The curve was fitted by the least square curve fitting with appropriate function for the interpolation of efficiency. The TENDL-2017 recommended cross-sections were used for the

Table 1 — Details of the observed reaction channels.

Reaction channel	Q value (MeV)	Gamma energy (keV) (I%)	Half-life	Efficiency	Abundance (%)	Decay constant ($\times 10^{-4} s^{-1}$)
^{54}Fe (γ, n)^{53}Fe	13.38	377.9 (42)	8.51m	0.01510	5.845	13.57
^{86}Sr (γ, n) ^{85m}Sr	11.11	231 (83.9)	67.63m	0.02738	9.86	1.7
^{64}Zn (γ, n)^{63}Zn	11.86	669.6 (8.2)	38.47m	0.00665	49	$3X10^{-4}$
^{85}Rb (γ, n)^{84m}Rb	10.48	248 (63)	20.26m	0.02257	72.17	5.7
^{55}Mn (γ, n)^{54}Mn	10.23	834.8 (100)	312.2d	0.00479	100	$2.6X10^{-4}$
^{35}Cl (γ, n) ^{34m}Cl	12.64	146.4 (38.3)	31.99m	0.04415	75.76	3.61
^{81}Br (γ, n) ^{80}Br		616.3 (6.7)	17.68m	.00746	49.31	65

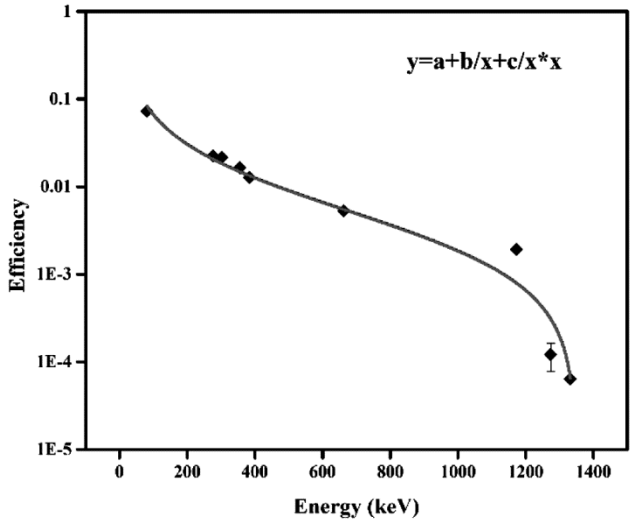

Fig. 1 — Efficiency calibration of CZT detector.

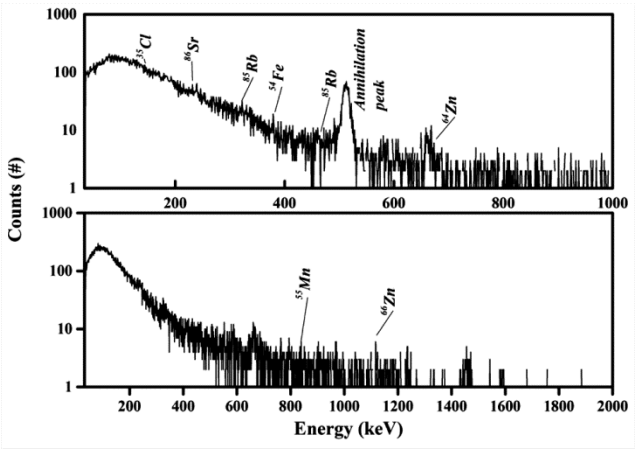

Fig. 2 — Spectrum for P. emblica for 10 m irradiation by Bremsstrahlung photons after 1.5hr (top) and 10 hr (bottom) cooling.

analysis, for both the sample as well as the monitor[16]. Half-life, gamma energy, intensity and abundance data were taken from the IAEA chart of nuclides[17]. The details of the observed reaction channels, gamma energies, half-life, efficiency, cross-section, decay constant and Q values are given in Table 1. Proper normalization has been done for energy averaged flux for different isotopes having different Q values using integral projection.

Table 2 — The concentration of trace elements obtained by photon activation method.

Elements	Reaction channel	Concentration ($mgkg^{-1}$)
Fe	^{54}Fe (γ, n)^{53}Fe	447 ±17
Sr	^{86}Sr (γ, n) ^{85m}Sr	50.6±7.9
Zn	^{64}Zn (γ, n)^{63}Zn	9.35±3.70
Rb	^{85}Rb (γ, n)^{84m}Rb	12.56 ±2.6
Cl	^{35}Cl (γ, n)^{34}Cl	71.67 ±14
Mn	^{55}Mn (γ, n)^{54}Mn	0.27±0.03
Br	^{81}Br (γ, n)^{80}Br	67.17±5.9

4 Results and Discussion

The efficiency calibration of the CZT detector was done using the standard sources. From the fitted curve, the energy-dependent efficiencies of the gamma lines corresponding to each element have been taken for the calculation. Typical bremsstrahlung spectrum at 20 MeV was used for the determination of integral flux.

A typical gamma-ray spectrum of P. emblica is shown in Fig. 2. The elemental identification was done from the centroid of the observed peaks. Accordingly, elements Like Fe, Sr, Zn, Mn, Cl, Br, and Rb were identified. For Rb, two peaks were identified at energies 248 keV and 464 keV resulting from the reaction ^{85}Rb (γ, n)^{84m}Rb. The spectrum showed an intense peak at 511 keV which can be attributed to pair annihilation. As the sample matrix is composed mainly of C, N and O whose (γ, n) reaction products are pure β^+ emitters which do not emit nuclide specific gamma rays but results in an intense annihilation peak.

The concentrations of individual isotopes in the sample have been calculated from the corresponding peak areas, and are given in Table 2. Out of the detected elements, Fe is found to be of highest

concentration. Cl, Fe, Zn and Mn are considered as the essential elements and play important roles in human body. The concentration of essential elements has to be at an optimum level for the proper cell functioning and homoeostasis. Many trace elements act as cofactors for enzymes. Fe is an important element in human body which enables the transport of oxygen from lungs to tissues. Deficiency of iron is responsible for anaemia which causes delayed growth in children and affects their cognitive development. Major elements like Na, K, Cl are responsible for fluid balance and pH maintenance in human body[18]. Rb is considered as non-essential element for human being, but it is found in micro gram levels in bones, soft tissues and muscles[19]. Zn is an important constituent of many enzymes[20]. Zn absorption is decreased by excess concentration of Fe[21]. Sr has a comparable ionic radius as Ca and has the same metabolic pathway. It is deposited in bone with more affinity towards areas of active growth and recent mineralization. Excess Sr in the human body is found to cause strontium rickets[22]. Toxic elements like Hg, Cd and As are found to be below detection limit in the sample.

The major and trace elements in *P. emlica* has been reported by different authors[23-26] employing different analytical techniques. The concentration of the reported elements available in literature varies significantly. Geographical and climatic factors can be attributed to the deviation of the concentration of elements in different reports.

This method can be used as a complementary tool to determine the trace elemental concentration in complex matrices. PAA can quantify trace elements like Sr which are difficult to quantify by conventional NAA either due to formation of stable daughter nucleus or due to less intensity or short half-life of daughter nucleus. The results from activation methods like PAA and NAA together with x-ray spectrometry can generate a complete elemental finger print of herbal samples in a non- destructive manner with high accuracy. This can be used for standardization of herbs and herbal products and preparation of reference materials.

5 Conclusions

The gamma activation analysis was employed for the determination of trace elements in *Phyllanthus emblica*. Seven trace elements were identified and their concentrations have been determined. Comparable results have been obtained for elemental concentration using different gamma energies of the corresponding element in the sample which reveals the accuracy of the method. High sensitivity with wide elemental range makes it a suitable candidate for characterization of samples with complex matrix. This method can be exploited as a non-destructive method that can complement other techniques to produce a complete elemental fingerprint of herbal formulations for quality assurance. The method of photon activation employing medical LINAC allows both qualitative and quantitative analysis of trace elements with reduced systematic errors in diverse sample matrices, which can be scaled to meet industrial and commercial needs.

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