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Abstract

Relative methods, which are performed with the assistance of reference materials, are widely used in photon activation analysis (PAA). On the contrary, absolute methods, which are conducted without any reference material, are rarely applied due to the difficulty in obtaining photon flux. To realize absolute measurement in PAA, we retrieve photon flux in the sample via Monte Carlo simulation and raise a novel procedure—quasi-absolute method. With simulated photon flux and cross section data from existing databases, it is possible to calculate the concentration of target elements in the sample straightforwardly. A controlled experiment indicates that results from the quasi-absolute method for certain elements are nearly comparable to relative methods in practice. This technique of absolute measurement has room for improvement in the future and can serve as a validation technique for experimental data on cross sections as well.

Full Text

Preamble

A Study of Quasi-Absolute Method in Photon Activation Analysis

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Abstract

Relative methods, which rely on reference materials for calibration, are widely used in photon activation analysis (PAA). In contrast, absolute methods, performed without any reference materials, are rarely applied due to the difficulty in determining photon flux. To enable absolute measurement in PAA, we retrieve photon flux at the sample position via Monte Carlo simulation and propose a novel procedure—the quasi-absolute method. Using simulated photon flux and cross-section data from existing databases, it becomes possible to calculate target element concentrations in samples directly. A controlled experiment demonstrates that for certain elements, results from the quasi-absolute method are nearly comparable to those obtained from relative methods in practice. This absolute measurement technique has room for future improvement and can serve as a validation method for experimental cross-section data.

Keywords: Photon activation analysis (PAA), Monte Carlo simulation, LINAC
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Introduction

Photon activation analysis (PAA) is, in most cases today, an accelerator-based radioanalytical technique. After irradiating samples with high-energy photons produced by bremsstrahlung radiation from electrons, qualitative and quantitative information about target elements can be obtained by detecting nuclear emissions. The first PAA publication dates back to 1951, when Gaudin and Pannell of MIT attempted to determine beryllium content in low-grade beryl ores through photodisintegration of beryllium [1]. They described this method as "rapid, simple, and nondestructive." In 1954, Basile proposed analyzing light elements using photonuclear reactions induced by bremsstrahlung radiation from a betatron [2], which led to widespread adoption of bremsstrahlung radiation as the high-energy photon source for PAA. A chapter in the *Encyclopedia of Analytical Chemistry* provides a brief yet comprehensive summary of PAA research [3].

In recent years, PAA has expanded its applications to radiotherapy, meteorology, geochemistry, archaeology, industrial materials, environmental studies, and other fields [4–10]. Figure 1 [Figure 1: see original paper] illustrates the basic principle of PAA. Photon activation typically occurs in the giant dipole resonance (GDR) region of the target nucleus. A high-energy photon above the particle emission threshold enters the nucleus and interacts with nucleons, causing the excited nucleus to equilibrate into a statistical "compound nucleus" state. This compound nucleus de-excites through the residual strong interaction by emitting prompt gamma rays, neutrons, protons, and even alpha particles. Following this stage, the product nucleus generally remains unstable because it is typically proton-rich or neutron-rich, continuing to de-excite to the final nucleus through weak interactions such as electron capture and beta decay. Delayed gamma rays are emitted after these weak interactions. In most PAA

studies, researchers focus on delayed gamma-ray emission with relatively long half-lives, which can be detected by HpGe spectrometers to generate spectra with computer assistance. The PAA procedure is thus straightforward: from delayed gamma-ray spectra, one acquires energy lines and intensities corresponding to specific product nuclides, then traces back to the quantity and species of target nuclides according to the corresponding nuclear reaction channels.

II. Calculations

According to Refs. [11-13], the net peak area (or counts) P of a characteristic gamma line in the spectrum is:

$$P = \eta\theta\zeta \int A(t)dt = \frac{\eta\theta\zeta m c_m h L}{A_r \lambda} \int_{t_i}^{t_i+t_c} (1-e^{-\lambda t_i})(1-e^{-\lambda t_c})e^{-\lambda t_d} \int_{E_{thres}}^{E_{max}} \phi(E)\sigma(E)dE,$$

where η is detector efficiency, θ is the branching ratio of the reaction channel, ζ is the absolute intensity of the gamma line, A is the activity of the radioactive nuclide, m is the total sample mass, c_m is the concentration of the nuclides of interest, h is the natural abundance of the target nuclide, L is the Avogadro constant, λ is the decay constant of the product nuclide, A_r is the atomic mass of the target nuclide, $\phi(E)$ is the energy-differential photon flux, $\sigma(E)$ is the cross-section of the photonuclear reaction of interest, t_i is irradiation time, t_c is counting time, and t_d is decay time from the end of irradiation to the start of spectrum collection.

Equation (1) can be rearranged as:

$$c_m = \frac{P A_r \lambda}{\eta\theta\zeta m h L(1-e^{-\lambda t_i})(1-e^{-\lambda t_c})e^{-\lambda t_d} \int_{E_{thres}}^{E_{max}} \phi(E)\sigma(E)dE}$$

On the left side of Eq. (2) is the concentration c_m of a certain element in the sample—the ultimate value PAA seeks. On the right side are mostly parameters we can measure (P, η, m, t_i, t_c, t_d) or find in existing databases (θ, ζ, h, L, λ, A_r, $\sigma(E)$). The only parameter we normally cannot measure directly is the energy-differential photon flux $\phi(E)$.

To find $\phi(E)$, we rely on computer simulations. From the simulated photon yield, it is feasible to derive photon flux and then calculate the concentration of the target nuclide directly using Eq. (2). The output of the computer simulation is the photon yield $Y(E)$. To obtain photon flux $\phi(E)$, one needs to multiply it by the average beam current I_{beam} of the LINAC as follows:

$$\phi(E) = Y(E) \times \frac{I_{beam}}{q_e}$$

where q_e is the charge of an electron. Inserting Eq. (3) into Eq. (2) yields:

$$c_m = \frac{PA_r\lambda q_e}{\eta\theta\zeta mhL(1-e^{-\lambda t_i})(1-e^{-\lambda t_c})e^{-\lambda t_d}I_{beam}\int_{E_{thres}}^{E_{max}} Y(E)\sigma(E)dE}$$

To simplify Eq. (4), we define the integral in the denominator as the reduced reaction rate I_R, transforming Eq. (4) into:

$$c_m = \frac{PA_r\lambda q_e}{\eta\theta\zeta mhL(1-e^{-\lambda t_i})(1-e^{-\lambda t_c})e^{-\lambda t_d}I_{beam}I_R}$$

In Eq. (5), uncertainties from atomic mass A_r, decay constant λ, electron charge q_e, detector efficiency η, branching ratio θ, absolute intensity ζ, natural abundance h, Avogadro' s number L, and time parameters (t_i, t_c, t_d) can usually be ignored. The primary sources of uncertainty are the net peak area P, sample mass m, beam current I_{beam}, and reduced reaction rate I_R. Hence, the uncertainty propagation of Eq. (5) follows:

$$\frac{\Delta c_m}{c_m} = \sqrt{\left(\frac{\Delta P}{P}\right)^2 + \left(\frac{\Delta m}{m}\right)^2 + \left(\frac{\Delta I_{beam}}{I_{beam}}\right)^2 + \left(\frac{\Delta I_R}{I_R}\right)^2}$$

One should note that the uncertainty of the reduced reaction rate in Eq. (6) combines the uncertainties of photon yield and cross sections.

III. Experimental Setup, Simulations, Cross Sections, and Photon Yield

A. Experimental Setup

The experiment to realize the quasi-absolute method was conducted using the 44 MeV L-band pulsed LINAC at the Idaho Accelerator Center. The experimental parameters were: peak current of about 300 mA, pulse width of 2.2 μs, repetition rate of 120 Hz, and peak energy of about 30 MeV. The side view of the experimental setup is shown in Fig. 2 [Figure 2: see original paper].

Electrons are first produced by a hot cathode and then accelerated by alternating RF electric fields in the acceleration cells, forming a focused electron beam through magnetic fields. The electron beam radius is approximately 3 millimeters. The energy distribution of the electrons (Fig. 3 [Figure 3: see original paper]) was measured with a Faraday cup, a magnetic spectrometer, and a beam-split to allow quasi-monochromatic electrons to pass after magnetic fields bend their trajectory.

After passing through a water cooling system and an air path, the electron beam is absorbed by a 3 mm-thick tantalum electron-photon converter (or radiator).

Bremsstrahlung radiation is the primary physical process in the radiator. After the radiator, the electron beam is almost completely stopped, and the newly generated photon beam strikes an aluminum hardener about 3 inches thick. The hardener absorbs residual electrons and ensures the beam exiting the radiator consists entirely of high-energy photons.

The urban particulate matter standard reference material 1648a [14] from NIST was chosen as the sample for verifying the quasi-absolute method. This material was selected because it is a well-characterized certified reference material widely used in instrumental analytical methods. The sample was wrapped into a 1 cm by 1 cm square area with aluminum foil and placed behind the hardener along the beam axis, with a thickness of about 1 mm.

B. Photon Beam Simulations

Photon flux simulation was based exactly on the geometry and materials of the experimental setup in Fig. 2. The simulated photon flux corresponds to the surface of the sample. Sample matrix effects (e.g., Compton scattering in the sample, gamma-induced further nuclear reactions) are not considered since the sample is small and thin. Geant4 was used as the primary simulation software, with MCNPX applied for ancillary validation. The Geant4 toolkit version applied to the simulation is 4.9.6 [15], using the Class Library of High Energy Physics (CLHEP) version 2.1.3.1 [16]. The Geant4 toolkit was installed on a 64-bit GNU/Linux computer server. The physics list for simulations includes all electromagnetic processes: ionization, multiple scattering, positron annihilation, photoelectric effects, Compton scattering, pair production, and bremsstrahlung radiation. In the simulations, the total number of electrons processed was 10 million, yielding small statistical uncertainty.

Figure 4 [Figure 4: see original paper] depicts the Geant4 simulation of a photon beam for the quasi-absolute method in PAA. In the figure, the yellow dot marks the tracking point. The relationship between track color and particle type is: photons—green, electrons—red, positrons—blue, neutrons—yellow. The yellow square disk at the end of the beam line represents the sample.

Figure 5 [Figure 5: see original paper] shows the difference between simulated photon yields from Geant4 and MCNPX using the same geometry and materials shown in Fig. 2. The two simulated results are consistent but exhibit slight variance. The percentage difference is approximately 2% for the entire energy range (0–30 MeV) and about 7.6% for the energy range of interest (10–30 MeV) in PAA. This discrepancy may originate from different cross-section libraries and different algorithms used to implement electromagnetic process calculations in the two simulation codes.

C. Selection of Cross Sections

Ten photonuclear reactions were selected for implementing the quasi-absolute method (see Table 2). They were chosen based on the following criteria: (1)

concentrations of their target nuclides are certified; (2) the target nuclides in this sample have a wide atomic number distribution from light to heavy elements; (3) their product nuclides have clear, interference-free energy lines (pile-up can be ignored at the low counting rates in these experiments); and (4) most are (γ, n) reactions. For a given isotope, the (γ, n) reaction channel has the largest cross sections in the GDR region.

Original cross-section data are in EXFOR format, which contains an extensive compilation of experimental nuclear reaction data [17–37]. These records were retrieved and validated via a consortium of organizations including the International Atomic Energy Agency (IAEA), the National Nuclear Data Center (NNDC), and the Center for Photonuclear Experiments (CDFE). Our criteria for selecting cross sections were: (1) find experimental reaction data and target isotopes as accurately as possible–(γ, n) data is preferred over (γ, total) and single target isotopes are preferred over targets with multiple isotopes; (2) the cross-section energy range should cover the energy range of interest (10–30 MeV); (3) the data should be as recent as available; and (4) data from highly relevant sources in nuclear physics were preferred.

D. Photon Yield

With proper cross-section data, we can apply the quasi-absolute method using Eq. (5) if photon yield is available. Photon yield was obtained from photon beam simulations as the ratio between the number of photons in a certain energy bin and the total incident electrons. The number of photons in different energy bins with varying sizes was counted using the "hist" function in statistical software R [38]. We tabulated the cross-section data and photon yield, then summed their products to obtain the reduced reaction rate I_R and its corresponding uncertainty. Table 1 provides an example of this process. In Table 1, E is energy, σ is cross section, $\Delta\sigma$ is cross-section uncertainty, "Energy Range" is the range centered on E, $N_p(E)$ is the number of photons in the energy range, $Y(E)$ is photon yield in the energy range, $Y(E)\sigma(E)$ is the reduced reaction rate in the energy range, $\Delta Y(E)\sigma(E)$ is the uncertainty of the reduced reaction rate in the energy range, and I_R is the total reduced reaction rate. After obtaining I_R and its uncertainty ΔI_R, we inserted them into Eq. (6) to calculate the estimated uncertainty for the quasi-absolute method.

IV. Results and Discussion

Table 2 shows the experimental results from the quasi-absolute method. In Table 2, h is natural abundance, E is the energy line used for calculation, $T_{1/2}$ is the half-life of product nuclides, Branch% is the absolute intensity of the energy lines, η is detector efficiency at that energy line, I is the reaction rate calculated from simulation and cross-section database, P is the net peak area, c is the NIST certified concentration value, c_q is the concentration calculated from the quasi-absolute method, and "accuracy" is the discrepancy between the two values. The uncertainty of the NIST certified value is expanded uncertainty with a coverage

factor of $k = 2$ (approximately 95% confidence) [14]. The uncertainty from the quasi-absolute method is calculated using standard uncertainty propagation formulas.

From Table 2, one can see that calculated values are close to certified values for Ca, Mn, Co, Ni, and Zn, but diverge for As, Rb, Sb, and Ce. The calculated concentrations are within a factor of two from the known concentrations. For some elements (e.g., As, Rb, Sb, and Ce), the quasi-absolute method results are considerably lower than the known concentrations—by nearly a factor of two. This may stem from the fact that the cross-section data applied to those isotopes are IAEA-tabulated total photonuclear cross sections. For several elements (e.g., Ca, Mn, Co, Ni, and Zn), the calculated concentrations are reasonably close to the known concentrations (around 20%). For zinc, two different reactions—(γ, n) and (γ, p)—yield very similar results. Additionally, our quasi-absolute method results are systematically lower, which could indicate that the simulated photon flux is higher than the actual flux. Many experiments have shown that simulated flux from standard Monte Carlo codes is higher than real experimental flux by approximately 20%, depending on different experimental setups and simulation programs [39–41]. This difference may arise from a combination of factors such as beam emittance, beam current uncertainty, beam loading, beam wandering, cross sections, energy dissipation in the experimental setup, etc.

Due to limitations in measuring experimental parameters, computer simulation of the bremsstrahlung photon beam, and cross-section data, the uncertainty of the quasi-absolute method may still be too high for practical use in precise radiochemistry and nuclear chemistry. In addition, the systematically higher photon flux from simulation is a source of systematic error in the quasi-absolute method.

V. Conclusion

We integrated absolute measurement calculations with bremsstrahlung photon yield simulation and investigated whether the quasi-absolute method could be developed and applied to practical radioanalytical chemistry. Experimental results show that the quasi-absolute method can be effective for some elements if cross-section data are accurate enough and simulated photon flux is close to real conditions.

The quasi-absolute method has merit in practice and considerable room for further improvement: after systematic adjustment of photon flux and more accurate measurements of experimental parameters (especially photonuclear cross sections), it may be possible to use the quasi-absolute method in actual radioanalytical practice for certain elements. Conversely, if we have a priori knowledge of elemental concentrations and a tagged photon beam, it is possible to invert the calculations to obtain valuable cross-section information. Theoretically, the quasi-absolute method will work well if measurements and corresponding simulations achieve the required precision and accuracy. This represents a valuable

direction in nuclear activation analysis.

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Note: Figure translations are in progress. See original paper for figures.