

Thermal-Neutron PGNAA-Based Elemental and Quantitative Composition Analysis of NCM Cathode Materials Using a High-Resolution LaBr₃(Ce) Scintillation Detector

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***Keywords :** PGNAA, LaBr₃(Ce), Thermal neutron, Prompt gamma-ray, HANARO

1. Introduction

With the rapid expansion of electric vehicle manufacturing and battery recycling infrastructures, non-destructive, real-time bulk assay of constituent elements in transition-metal mixtures—specifically Lithium Nickel-Cobalt-Manganese oxides (NCM) and shredded black mass—has become increasingly vital. Conventional chemical characterization methods, such as Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Atomic Emission Spectrometry (ICP-AES), provide high sensitivity but require destructive, hazardous, and time-intensive acid dissolution procedures.

Prompt Gamma Neutron Activation Analysis (PGNAA) offers an effective alternative, exploiting the deep penetrating capability of thermal neutrons and multi-MeV prompt gamma-rays to perform bulk, in-situ, non-destructive elemental quantification without complex sample pre-treatment. However, the prompt gamma-ray spectra of transition-metal mixtures are densely populated with closely spaced photopeaks and significant Compton continuum baselines.

To overcome severe peak-overlap limitations inherent to conventional scintillators while preserving high-count-rate tolerance, this work evaluates the spectroscopic capability and quantitative deconvolution performance of a LaBr₃(Ce) detector system. Thermal-neutron activation experiments were performed at the HANARO to benchmark elemental identification fidelity and quantitative mass-fraction estimation across pure, binary, and ternary NCM (NCM622 and NCM811) cathode transition-metal matrices.

2. Materials and Methods

2.1 Experimental Setup and DAQ system

PGNAA measurements were conducted at the Four-Circle Diffractometer (FCD) beamline of the HANARO (KAERI). As illustrated in Fig. 1, samples placed in cylindrical containers (radius = 2.75 cm, height = 8.0 cm) were aligned at a 90° orientation relative to the incident beam, with a sample-to-detector distance of 40 cm.

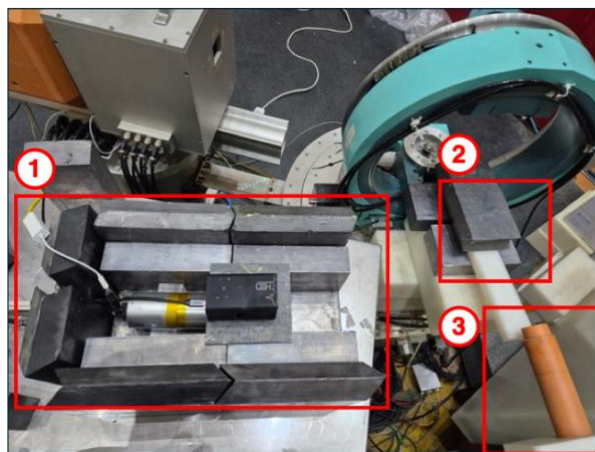


Fig. 1. Experimental configuration at the HANARO four-circle diffractometer. ① Detector position, ② sample position, and ③ thermal-neutron beamline

To suppress pulse pile-up and saturation under high-count-rate conditions, the preamplifier was eliminated; PMT anode signals were directly processed using a CAEN N1068S shaping amplifier ($\tau = 0.5 \mu\text{s}$, Coarse Gain: 8, Fine Gain: 10) and digitized via a 16K-channel ADC (CAEN N6741). Targets included pure metals (Mn, Fe, Co, Ni) and ternary transition-metal mixtures approximating NCM622 and NCM811, each measured for 900 s with dead time <10%.

2.2 Spectral and Quantitative Analysis

For qualitative and quantitative evaluation, candidate peaks were first detected in the raw channel domain via Gaussian derivative convolution (Becquerel library) to eliminate calibration error propagation, and statistically validated against the IAEA prompt gamma-ray database using SNIP baseline subtraction and the Currie decision limit [1]. Subsequently, elemental mass fractions in the mixed targets were determined by deconvoluting the net count-rate spectra with a pure-element response library using Poisson-weighted non-negative least squares (WNNLS) with Tikhonov regularization, incorporating element-wise axial neutron self-shielding and gamma-ray attenuation corrections [2].

3. Results and Discussion

3.1 High-Fidelity Elemental Identification Performance

In single-element standard runs, the $\text{LaBr}_3(\text{Ce})$ detector preserved 13 statistically significant sample-added peaks for Co after SNIP-Currie filtering. Primary characteristic lines for Mn (212.0 keV), Fe (136.5 keV), Co (277.2 keV), and Ni (878.0 keV) were identified with tight centroid deviations ($\Delta E < 9.0$ keV) and high statistical significance ($Z = 11.66 - 68.02$).

In multi-component NCM mixtures, where primary gamma lines experience severe spectral crowding, the superior intrinsic resolution of $\text{LaBr}_3(\text{Ce})$ allowed clear separation of the Co multiplets (229.9, 277.2 keV) and Ni signatures (282.9, 878.0 keV), achieving an unambiguous "High" identification reliability rating across all samples.

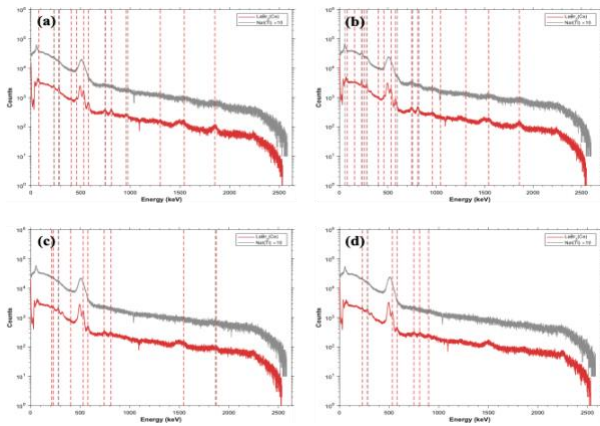


Fig. 2. Prompt gamma-ray spectra and identified peaks for target samples: (a) Co, (b) Fe-Co, (c) NCM622, and (d) NCM811.

3.2 Quantitative Composition Deconvolution for NCM622 and NCM811

The quantitative deconvolution for the Ni-Co-Mn 6:2:2 target (nominal 60.0 wt.% Ni, 20.0 wt.% Co, and 20.0 wt.% Mn) was performed using regularized WNNLS. As shown in Fig. 3, applying the axial attenuation correction to the $\text{LaBr}_3(\text{Ce})$ response matrix improved estimation accuracy, yielding 55.1 wt.% Ni, 24.3 wt.% Co, and 20.6 wt.% Mn (deviations of -4.9, +4.3, and +0.6 %pt, respectively).

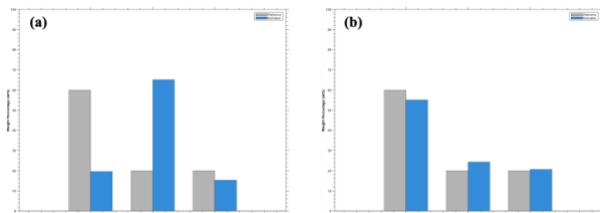


Fig. 3. Estimated mass fractions (wt.%) for the Ni-Co-Mn 6:2:2 mixture using $\text{LaBr}_3(\text{Ce})$: (a) WNNLS and (b) WNNLS + simplified attenuation correction.

For the asymmetric Ni-Co-Mn 8:1:1 mixture (nominal 80.0 wt.% Ni, 10.0 wt.% Co, and 10.0 wt.% Mn), the system effectively extracted dilute minor components from the dominant Ni matrix. As shown in Fig. 4, the attenuation-corrected deconvolution yielded 77.1 wt.% Ni, 11.0 wt.% Co, and 11.9 wt.% Mn (deviations of -2.9, +1.0, and +1.9 %pt), resulting in an improved mean absolute error of 1.9 %pt and $\text{SR}^2 = 0.9970$. This confirms that the superior energy resolution of $\text{LaBr}_3(\text{Ce})$ robustly preserves weak minor-element lines in asymmetric cathode matrices.

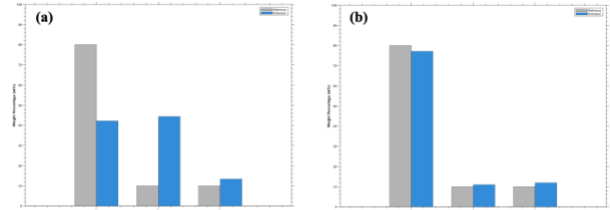


Fig. 4. Estimated mass fractions (wt.%) for the Ni-Co-Mn 8:1:1 mixture using $\text{LaBr}_3(\text{Ce})$: (a) WNNLS and (b) WNNLS + simplified attenuation correction.

4. Conclusions

This study demonstrated the viability and precision of a high-resolution $\text{LaBr}_3(\text{Ce})$ detector system for thermal-neutron PGNA of secondary battery cathode materials at the HANARO. By integrating a fast preamplifier-less DAQ chain, SNIP-Currie automated peak validation, and regularized WNNLS deconvolution, the platform robustly quantified NCM622 and NCM811 mass fractions with a mean absolute deviation of 1.9–3.3 %pt.

Acknowledgements

This work was supported by the KAERI Project (project no. 523160-26)

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