

Development and Evaluation of an External Standard Method for k_0 -Based Neutron Activation Analysis of Ancient Pottery

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***Keywords :** Neutron Activation Analysis, Analytical conditions, Quantitative method, k_0 , Pottery

1. Introduction

Pottery is produced from geological raw materials, and its chemical composition reflects their mineralogical and geochemical characteristics. Trace elements show geographical variation while remaining relatively stable and immobile [1], making them useful fingerprints for investigating provenance, raw-material supply, and exchange networks [2]. Neutron Activation Analysis (NAA) quantification is affected by various factors, including the neutron field, irradiation and decay conditions, detector characteristics, etc. Different quantification schemes have therefore evolved according to how these factors are incorporated into the calculation. Among these approaches, k_0 standardization method was developed to address the uncertainties associated with the absolute method and the dependence of the relative method on reference materials [3].

In NAA studies on ancient pottery, the quantification procedure is not clearly specified in all research, and comparatively little attention has been given to selecting an analytical method appropriate for the characteristics of cultural heritage materials. Pottery studies commonly involve repeated measurement of many specimens and comparison of compositional differences among them. Thus, method selection should consider these characteristics. On this basis, the present study proposes a new k_0 -based external standard method for future pottery analysis and compositional database construction.

2. Methods and Results

2.1 Materials

Geological reference materials with matrix comparable to pottery were selected for this study. These materials were produced by the Geological Survey of Japan and represent a range of rock and mineral types, including andesite, basalt, and feldspar.

2.2 Methods

Four analytical conditions with different sample masses and experimental times were first established,

and each element was assigned to the condition that minimized counting-related uncertainty. Preparatory steps were then carried out for the external standard method. Finally, its quantitative performance was evaluated against the conventional methods.

NAA was conducted at the HANARO research reactor of the Korea Atomic Energy Research Institute (KAERI) at a thermal power of 27 MWth. Four irradiation conditions were established using two pneumatic transfer system (PTS) positions, with neutron fluxes of 3.28×10^{13} and 2.48×10^{13} $\text{cm}^{-2} \text{s}^{-1}$, respectively. Gamma-ray spectra were acquired using a high-purity germanium (HPGe) detector coupled with a 16k multichannel analyzer (MCA).

3. Results

The analytical conditions used in this study are summarized in Table 1. Three spectra were acquired for each geological reference material under identical conditions, and the mean count and standard deviation were calculated for each element. These values were then applied to a newly developed index in this study. The index was defined as the mean count from three measurements divided by the product of the standard deviation and counting time. For each element, the analytical condition to be adopted was determined based on the frequency with which each condition was identified as the most suitable among all samples ($n = 13$), as shown in Fig. 1. The resulting element-specific condition assignments are presented in Table 2.

Table I: Analytical Conditions According to the Half-Lives of the Radionuclides

	Short-Lived		Medium/Long-Lived	
Condition	1	2	3	4
Sample mass	20 mg		50 mg	
Irradiation	10 s		2 h	
Cooling	15 m	17 m	7 d	14 d
Measurement	120 s	1200 s	4800 s	7200 s

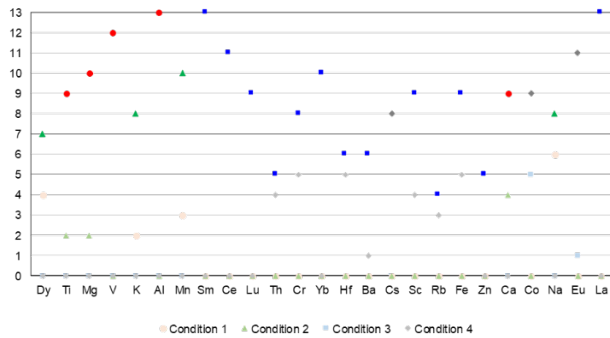


Fig. 1. Frequency of each analytical condition being evaluated as optimal.

Table II: Elements Assigned to Each Analytical Condition

Condition	Elements
1	Ti, Mg, V, Al, Ca
2	Dy, K, Mn, Na
3	Sm, Ce, Lu, Th, Cr, Yb, Hf, Ba, Sc, Rb, Fe, Zn, La
4	Cs, Co, Eu

The external standard method combines concepts from the single comparator and internal mono standard approaches of k_0 standardization. The analytical sample and a reference material with a similar matrix are treated as one analytical set. And specific elements in the reference material serve as the comparator for quantification. Na and Co were identified as suitable elements.

The conventional methods and external standard method were finally applied to three geological reference materials. Regression slopes and coefficients of determination were compared between measured and certified concentrations. For all three materials, the external standard method yielded values closest to the ideal regression criteria, as shown in Fig. 2. Fig. 3 also shows that the concentrations quantified using the external standard method were generally close to the certified values for all three samples.

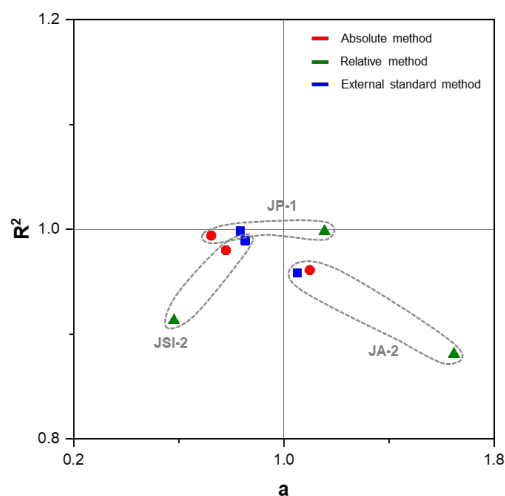


Fig. 2. Comparison of regression slopes and linearity of three quantification methods

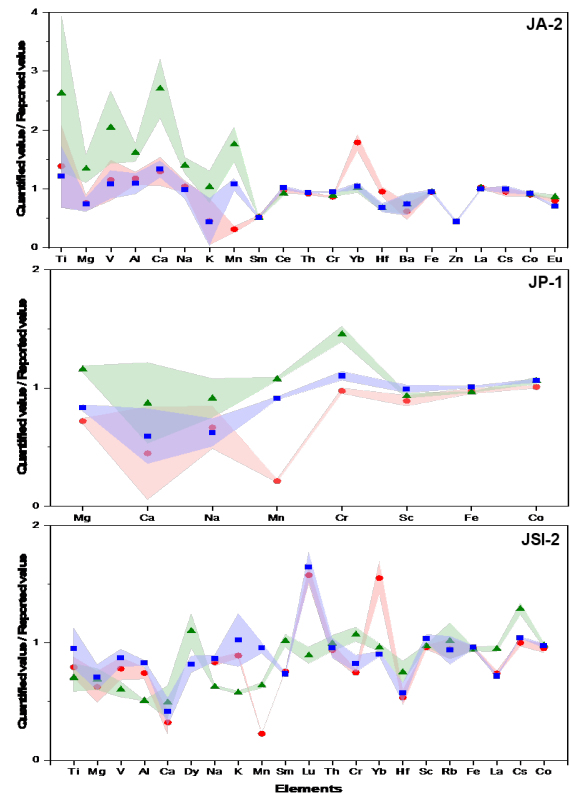


Fig. 3. Comparison of the ratios of quantified to certified values for three quantification methods.

4. Conclusions

The newly proposed external standard method exhibited strong quantitative performance when applied to geological reference materials. Its ability to determine a wide range of elements above their detection limits, while facilitating repeated measurements and concurrent quality control, indicates its suitability for pottery analysis.

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