Development of Synthetic Calibration Standards for X-ray Fluorescence Determination of Japanese Ancient Pottery

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X-ray fluorescence spectrometry (XRF) is routinely employed for the determination of major and minor elements in solid and powdered samples in many different fields of study. Ancient pottery in archeology is one of them. Generally, calibration curves of XRF determination have been drawn by commercial references or synthetic calibration standards. The commercial references have limited chemical compositions, so that the calibration curves constructed from them might produce erroneous results due to the following factors: (1) irregular bias of the plot interval; (2) overly large or small calibration range; and (3) matrix effects caused by the differences in chemical composition among the reference and target samples. In contrast, synthetic calibration standards prepared from chemical reagents containing each target analyte can provide appropriate calibration curves that are customized for a given sample type. In this study, synthetic calibration standards were developed for determination of major oxides (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, and Fe_2O_3) and minor elements (V, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, and Pb) in Japanese ancient pottery. Compositions of the standards were determined based on compositional characteristics of Japanese potteries. Furthermore, reliability of calibration curves using the present standards was validated by geochemical references issued by the Geological Survey of Japan (GSJ).

One hundred sixty-six ancient potteries from various area in Japan were prepared as glass bead specimens with 1:10 sample-to-flux ratio and analyzed by fundamental parameter method/XRF calibrated with six geochemical references (JSd-1, JSd-2, JSd-3, JB-1a, JG-3, and JR-2) issued by GSJ. Synthetic calibration standards were glass beads (sample-to-flux ratio = 1:10) made from 22 chemical reagents containing each analyte and alkali flux. Preparation method of these specimens were described in detail elsewhere[1].

Two-dimensional scatter diagrams using XRF results of the potteries indicated the following compositional characteristics: SiO_2 had positive corrections with K_2O, P_2O_5, Rb, Y, Zr, Nb, Ba, and Pb and negative corrections with Na_2O, MgO, Al_2O_3, CaO, TiO_2, MnO, Fe_2O_3, V, Cr, Ni, Cu, Zn, and Sr. Compositions of each standard were determined in imitation of the characteristics. The weight of each reagent for the standards was calculated from concentrations of the analytes, *i.e.*, oxide form for major elements and metal form for minor elements. The XRF calibration curves constructed by the standards, showed good linearity with $r > 0.997$. For validation, three geochemical references (JSd-1, JSd-2, and JSd-3) were analyzed using the present calibration curve method. The analytical results were good agreement with the references. Therefore, the present method may enable to provide reliable chemical compositions of pottery samples, making it useful for the study of provenance.

[1] S. Ichikawa, T. Matsumoto, T. Nakamura: *Anal. Methods*, **8**, 4452 (2016).