X-ray fluorescence analysis with micro-glass-beads using one-milligram of archaeological samples for application to determination of minor elements

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A micro-glass-bead (around 3.5 mm diameter and 0.8 mm height) technique using a minimum amount (1.1 mg) of powdered sample was developed for the X-ray fluorescence analysis (XRF) of ten major oxides (Na$_2$O, MgO, Al$_2$O$_3$, SiO$_2$, P$_2$O$_5$, K$_2$O, CaO, TiO$_2$, MnO, and total Fe$_2$O$_3$) and four minor elements (Ni, Zn, Rb, and Sr,) in precious and limited silicic samples, e.g., archaeological ceramics, rock, mineral, sand, clay, and sediment in geochemistry and archaeology.

The micro specimen [1] was prepared with 1.10 ± 0.05 mg of powdered sample and 11.00 ± 0.05 mg of anhydrous lithium tetraborate as an alkali flux. The specimen was produced by following method s : (1) 10 μl of 1.84 mass%-lithium chloride solution was dropped on a center of commercial platinum crucible (35 mm diameter) as a releasing agent; (2) a mixture of the sample and the flux was added to the liquid-drop; (3) the wet mixture was dried at 110°C for 5 min; (4) the dried mixture was preheated at 800°C for 60 s, molten at 1000°C for 60 s, and shaped in a circle at 1000°C; and (5) a hemispherical melt was vitrified by air-cooling, and the glassy product was released from the crucible using a stainless-steel spatula. The micro-glass-bead was bonded on a 35 mm glass bead blank sample (produced by mixing the flux with the releasing agent), and then, X-ray intensities of Kα lines from the each analytes were measured by a wavelength-dispersive XRF spectrometer (RIX3100, Rigaku Corp.). A receiving diaphragm was 3 mm diameter.

Synthetic calibration standards were prepared by compounding chemical reagents; calibration curves showed good linearity with correlation coefficient values of more than 0.992. The fourteen components in three geochemical reference samples, JB-1a (basalt), JR-3 (rhyolite), and JSd-2 (stream sediment) issued by the Geological Survey of Japan, were determined to validate the proposed technique. The results were mostly agreed with the recommended values. The developed technique was applied for analyses of two ancient potteries and obsidian. The grate advantage of this micro-sized method is that only a very small amount (1.1 mg) of sample is required for XRF determination with destructive sample preparation.