

## fsLA-ICPMS analysis of XRF glass beads

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Analysis of naturally heterogeneous rock samples by ICP-MS requires laborious sample preparation including acid/alkali digestion. Crystalline plutonic rocks or sediments remains as challenging analysis by ICP-MS because of the difficulty in complete digestion of acid resistant minerals which contain significant fraction of high field strength elements (HFSE) or rare earth elements (REE). We tested femto-second laser ablation (fsLA) ICP-MS analysis of glass beads prepared for X-ray fluorescence spectrometry (XRF). This method maintains benefits of no sample digestion by wet chemistry, high sensitivity, high sample throughput and low costs. A comprehensive examination of measurement parameters was made on wave length and repetition rate of the laser beam. Choice of internal standard and external calibration method were also examined. Using high-diluted glass beads (1:10 sample to lithium tetraborate ratio) and optimized in-house developed fsLA system coupled to a quadruple-type ICP-MS (iCAP Qs, ThermoFisher Sci.), the parameters and methods were validated by determining 48 elements including ten major (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P), refractory lithophile (Sr, Ba, REE and HFSE) and volatile (Ga, Rb, Cs, Tl, Pb) elements in well-established geological reference materials (GSJ JB-1, JG-1a, JG-2 and JR-1) and synthetic reference glasses (NIST SRM 612, USGS GSD-1G). Laboratory bias (or trueness by ISO 5725-1) for most elements was better than 10% when compared to the reference or consensus values. Poorly determined or failed elements were P, Sc, V, Ni, Sn, Sb, and W, whose data deviated from the reference values >20%. Volatile elements such as Rb, Cs and Ga showed no substantial loss; however, Tl and Pb exhibited always lower values suggesting their loss during fusion in the glass bead preparation. Repeatability and intermediate precision (ISO 5725-1) of all measured elements were better than 5–7% RSD except Cu, Sn, Sb, Cs and Tl which showed 10–40% RSD due to extremely low abundances or strong spectral interferences. The low limits of detection by this method were comparable to those obtained by solution ICP-MS for most elements of geochemical interests. Our results demonstrate that the fsLA-ICPMS using XRF glass bead can be used for rapid bulk-rock analyses of trace, minor and major elements.

Keywords: femto-second LA-ICP-MS, bulk analysis, XRF glass bead, geological reference materials