Matrix-Independent Calibration of Laser Ablation Microanalysis by High Resolution ICP-MS

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The combination of laser ablation and inductively coupled plasma mass spectrometry (LA-ICPMS) allows for rapid chemical analysis of solid samples at high spatial resolution. Calibration of the technique is limited by the small number of reliable standards available and by the diversity of solid matrices, including silicates, oxides, sulfides, carbonates, metals, etc. The situation is best for silicate glasses, for which both USGS standards and MPI-DING glass standards are available spanning a wide range of silica content. In laser ablation, the laser produces an aerosol that is ionized by the argon plasma source, so that ionization efficiency depends primarily on the plasma and not on the ablation process. Thus, internally standardized measurements by laser ablation should, in principle, be insensitive to matrix composition. Concerns about the necessity for sample-standard matrix matching have previously limited the possible quantitative applications of the method, but the necessity of matrix matching has not been previously studied in detail. We will present the results of a detailed study of matrix-dependence on inter-calibration of a broad range of elements in silicate, sulfide, metal and aqueous matrices, using a UP213 (213 nm) laser ablation system coupled to high resolution ICP-MS (Element1 and Element XR). We define a relative sensitivity factor (RSF) for each element which, when multiplied by the ion intensity ratio, yields a concentration ratio to an internal standard element. This study documents that the RSFs for practically all elements with a First Ionization Potential (FIP) below 8 ev are matrix-independent. The calibration of laser ablation analysis of such elements can be performed using aqueous or desolvated aqueous standards. Finally, using the faraday cup detector of an Element XR, we examine the influence of the measured oxygen and argon ion intensities on the RSFs of other elements. We find that as the oxygen ion to argon ion ratio increases, the RSF of high FIP elements increases (i.e., measured intensity decreases). Thus, for such elements the decrease of measured ion.
intensity is coincident with increased oxygen ion production in the plasma (most notably for aqueous matrices), and this constitutes a true matrix effect for ICP-MS analysis.