External mass bias correction of $^{208,207,206}Pb/^{204}Pb$ ratios applying non-linear calibration

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Accurate lead isotope determinations by LA-ICP-(Q, SF, MC)-MS are often limited to $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ because of the low abundance of ^{204}Pb and isobaric interference by ^{204}Hg related to the presence of Hg in the carrier and plasma gas, respectively. An external correction for mass discrimination of ^{204}Hg-corrected $^{208,207,206}Pb/^{204}Pb$ ratios using reference materials such as NIST SRM 612 ([Pb] = 38.57 μg/g) yields ^{204}Pb ratios for materials with Pb concentrations <10 μg/g which are too low by several percent. The most plausible explanation is an undercorrection of mass 204 caused by isobaric interferences additionally to the ^{204}Hg interference revealing a negative relationship between Pb concentration and magnitude of undercorrection. In this study, measurements were performed using a NWR193 ArF excimer laser system coupled to an Agilent 7500ce quadrupole ICP-MS. To determine a calibration curve for the external correction of $^{208,207,206}Pb/^{204}Pb$ ratios, reference glasses (NIST SRM 612, MPI-DING KL2-G, GOR132-G, StHs6/80-G, ML3B-G, ATHO-G and T1-G, and USGS GSD-1G, BIR-1G, and BCR-2G) were analyzed. On each material ([Pb] = 1.38–50 μg/g) five spot analyses were performed. The correction factors were calculated for each reference material by dividing the measured ratio by its "true" ratio. The relationship between Pb concentration or count rate of ^{208}Pb and correction factors can be described either by a power law or an exponential function. For unknown samples the average count rate of ^{208}Pb obtained during the measurements is used to calculate the respective correction factor. To test the potential of this approach, reference materials (NIST SRM 614, USGS NKT-1G and NIST SRM 1400; [Pb] = 2.32–9.07 μg/g) with known Pb isotopic composition were analyzed as unknown samples. Measured $^{208,207,206}Pb/^{204}Pb$ ratios of the low-Pb materials yield a precision of 0.5–2 % (1RSD) and correspond with published values considering analytical uncertainties. $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios agree with published high-precision TIMS and MC-ICP-MS data within the external precision of typically <0.8 % (1RSD). The presented data indicate that the described approach is a suitable tool for the determination of $^{208,207,206}Pb/^{204}Pb$ related to geological or geochemical questions in cases where more complex high-precision TIMS or MC-ICP-MS are not necessarily required.