Ion counter nonlinearities

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Time-independent nonlinearities in ion counters (IC) are long known. Nonlinear gain (e.g. Richter et al, Int J Mass Spec 206 (2001) 105) and dead time can be individually charted. They must be accounted for in uncertainty estimates. The IC gain is assumed constant over time.

We observed a time-dependent nonlinearity, "slow Wake-up" (sWu) of our ETP™ multiplier. A similar effect is known for photomultipliers (Philips Photonics (1994) Photomultiplier tubes - principles and applications, 203 p). Hour-scale drifts were reported by Turrin et al (G-cubed 11 (2010) Q0AA09). We acquired two ion beams simultaneously, on the Faraday cup (F) and the IC, during 50 blocks, each of 3 s baseline and 3 on-peak measurements of 1 s each. Total run times for this protocol were 900 s. We observed an asymptotic increase of the IC/F gain $G = g_0 + g_1*(1-\exp(-t/\tau))$, g_1 being 1-7 % of g_0, and τ between 50 and 200 s. The sWu is slowest (g_1 and τ highest) after weekends and idle periods; even half-hour breaks between runs slow down the sWu. The sWu can be misdiagnosed as "normal" tube memory if run times are less than 3-4 τ, or IC integration times are >> 1 s, or both.

These observations were reproduced on a multicollector ICP. By measuring the ratio of the $^{40}Ar_2$ dimer on a Faraday cup to the $^{36}Ar^{40}Ar$ dimer on an ETP IC with a 1 s time resolution we found a sWu with $g_1 = 0.02*g_0$ and $\tau \approx 15$ s. This is not visible with our usual protocol involving 10 s integration time, and/or mistaken as random plasma oscillation. In hindsight, the MasCom™ multiplier of a dual-collector MAP 215 formerly in use in Berne almost certainly suffered from sWu, with $\tau \approx 10$ s.

To assess the general importance of undiagnosed sWu, we simulated zero-time extrapolations for (i) multicollector (F + IC), (ii) single-collector, ion-counter-only mass spectrometers. Case (i) always gave an inaccurately low regression of the isotope measured on the slow IC. Case (ii) always gave inaccurately low regressions for all isotopes, but the inaccuracy effect on calculated ages is opposite if the measuring sequence is decreasing (40 to 36) or increasing (36 to 40). The workaround solution to this systematic bias is acquiring long runs ($t > 5\ \tau$) with 1 s integration times.