Background correction for clumped isotope analysis of CO_2 based on m/z = 49 ion beam intensities

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It has been well reported that a subtle non-linearity can occur during gas source mass spectrometry that - if remaining unaddressed - limits accuracy of CO_2 clumped isotope analysis [1]. This is expressed by a negative background on the m/z = 47 Faraday cup, whose magnitude inversely correlates with the m/z = 44 signal [2, 3]. In order to correct for this effect, equilibrated gases with known bulk and clumped isotopic compositions are commonly measured along with the samples and the m/z = 44 signals of the reference and sample gas are closely adjusted to identical intensities. Time consuming measurements of heated gases can be reduced if the intensity of the m/z = 44 ion beam and the corresponding negative background on m/z = 47 can be monitored simultaneously, such that measured m/z = 47 beam intensities can be corrected for the contribution of secondary electrons [3]. We present another correction procedure that is based on simultaneous monitoring of m/z = 49 ion beam intensities and corresponding m/z = 47 “off-peak“ backgrounds, both for the reference and the sample gas, prior and after each acquisition. Our first results imply that background corrected data does not exhibit any significant non-linearity anymore and that precision occurs improved relative to uncorrected data. Our proposed background correction scheme can be applied if the slit widths of the m/z = 49 Faraday cup is bigger than that of the m/z = 47 cup.

[1] Huntington *et al* (2009), *J. Mass Spectrom.* **44**, 1318-1329; [2] He *et al* (2012) *Rapid Commun. Mass Spectrom.* **26**, 2837-2853; [3] Bernasconi *et al* (2013), *Rapid Commun. Mass Spectrom.* **27**, 603-612.