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On the interference of Kr during carbon isotope analysis of methane using continuous-flow combustion–isotope ratio mass spectrometry

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Stable carbon isotope analysis of methane (δ^{13}C of CH_4) on atmospheric samples is one key method to constrain the current and past atmospheric CH_4 budget. A frequently applied measurement technique is gas chromatography isotope ratio mass spectrometry coupled to a combustion-preconcentration unit. This report shows that the atmospheric trace gas krypton can severely interfere during the mass spectrometric measurement leading to significant biases in δ^{13}C of CH_4 if krypton is not sufficiently separated during the analysis. According to our experiments, the krypton interference is likely composed of two individual effects with the lateral tailing of the doubly charged ^{86}Kr peak affecting the neighbouring m/z 44 and partially the m/z 45 Faraday cups. Additionally, a broad signal affecting m/z 45 and especially m/z 46 is assumed to result from scattered ions of singly charged krypton. The introduced bias in the measured isotope ratios is dependent on the chromatographic separation, the Kr to CH_4 mixing ratio in the sample, the mass spectrometer source tuning as well as the detector configuration and can amount to up to several permil in δ^{13}C. Apart from technical solutions to avoid this interference we present correction routines to a posteriori remove the bias.