Measuring the chlorine and carbon isotopic composition of chlorofluorocarbons

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Methodologies for the unconventional use of gas chromatography-mass spectrometry (GC-MS) have been developed to determine the $\delta(^{37}Cl)$ and $\delta(^{13}C)$ values of chlorinated halocarbons using a triple-sector single detector GC-MS. These methodologies are described here as applied to the three most common CFCs (CFC11, -12 and -113). Measurements have been achieved in small (200 cm^3) air sample sizes and at low mixing ratios (a few ppt). Careful attention is required to the analytical parameters to optimise the mass chromatographic peak size while minimising interferences from other atmospheric constituents. Care is also required to avoid or account for non-linearities that occur at very low abundances. Measurement uncertainties of around 2 – 3 ‰ (1-σ) were obtained for both chlorine and carbon isotope ratios and in all three CFCs, after a series of optimisation procedures were implemented. The method has been used to measure a time series of ratios in air samples from Cape Grim and older air from polar firn air. Over the period of measurements there was no detectable change in the isotope ratios, but the method offers promise for detecting potential differences in source signatures.