



The Sercon CryoGas: for automated, high precision $\delta^{2}\text{H}$ and $\delta^{13}\text{C}$ analysis of gaseous and dissolved methane

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Atmospheric methane (CH_4) is one of the most abundant and potent greenhouse gases. As concentrations in the atmosphere have more than doubled since pre-industrial times (Etheridge et al., 1998; Fisher et al., 2006), understanding methane formation pathways and sources of emission is critical to informing effective mitigation strategies and limiting the role of methane in future climate change. Alongside impacts within the atmosphere, high concentrations of dissolved methane in groundwater (Bell et al., 2017) pose a significant risk to human health. Recent investments in the shale gas industry have meant that fingerprinting methane sources within groundwater is becoming a critical concern for operators and regulators alike (Bordeleau et al., 2015; Osborn et al., 2011).

The dual isotope analysis, hydrogen ($\delta^{2}\text{H}$) and carbon ($\delta^{13}\text{C}$), of methane is a key tracer tool for understanding sources, mixing and evolution of both dissolved and atmospheric methane. However, traditional methods of analysing methane for $\delta^{2}\text{H}$ and $\delta^{13}\text{C}$ are very time consuming; involving offline, manual extractions. This processing time can drastically reduce the number of analyses that can be undertaken, often limiting the scope of long term dual isotope monitoring. Here we describe a new gas chromatography, pyrolysis/combustion, isotope ratio mass spectrometer system for the automated analysis of CH_4 down to ambient atmospheric concentrations (1800ppb). Sample introduction is via a traditional XYZ auto sampler, allowing helium purging of either gas or “sparging” of water from a range of airtight bottles. The system routinely achieves precision of $<0.1\text{‰}$ for $\delta^{13}\text{C}$ and $<2.5\text{‰}$ for $\delta^{2}\text{H}$. Depending upon CH_4 concentration and therefore bottle size, the system runs between 16 and 150 unknowns in an unattended run overnight. This system currently represents the only commercially available IRMS system for dual hydrogen and carbon isotope analysis of methane and a step forward for the routine analysis of CH_4 in environmental studies.

Bell, R.A., (2017), *Sci. Total Environ.* 601–602, 1803–1813. Bordeleau, G., (2015), *Procedia Earth Planet. Sci.* 13, 219–222. Etheridge, D.M., (1998), *J. Geophys. Res.* 103, 15,979-15,993. Fisher, R., (2006), *Rapid Commun. Mass Spectrom.* 20, 200–208. Osborn, S.G., (2011), *Proc. Natl. Acad. Sci.* 108, 8172–8176.