Appendix E

Mass Spectrometry: Analysis and Calibration
E.1 Mass Spectrometers

Three dual-inlet mass spectrometers were used during this research. CO₂ isotopic ratio determination was achieved at Royal Holloway University of London on VG Prism and Optima mass spectrometers. The H₂O produced by the new cryogenic extraction line was reduced to H₂ and analysed at The University of East Anglia (Environmental School, Stable Isotope Laboratory) on a VG 602D.

E.2 Isotopic Notation

To summarise: the notation for reporting stable isotopic measurements is calculated by equation D.1 (from Craig 1957). This example given is for carbon isotope measurements. The equivalent for hydrogen is ²H/¹H. The labels STD and SAM are abbreviations for standard and sample respectively.

\[
\delta^{13}C = \left[ \frac{^{13}C / ^{12}C_{SAM}}{^{13}C / ^{12}C_{STD}} - 1 \right] \times 10^3 \text{ or per mil (‰)} \quad \text{Equation E.1}
\]

E.3 Preparation of CO₂ and H₂O for Analysis

The reduction of H₂O to H₂ gas is fully documented in Chapter 6. The method of preparation of CO₂ gas before expansion into either Prism or Optima mass spectrometers is summarised below:

- The CO₂ produced by the new cryogenic extraction line is stored in sample bottles with PTFE valves seals on glass stems. These bottles are attached to the inlet port of the mass spectrometer.

- The inlet port of the Prism has been designed at RHUL to connect with an additional pumping system so that high vacuum can be achieved without using the mass spectrometer pumps. This allows the CO₂ gas in
the sample bottle to be prepared prior to expansion into the mass spectrometer inlet system.

- The CO₂ sample is transferred by liquid nitrogen to a glass ‘finger’ on a secondary line. This system is backed with both rotary and diffusion style pumps allowing a vacuum in the range of 10⁻⁵ mbar to be maintained. The glass finger is evacuated whilst the CO₂ remains frozen. This removes remaining non-condensable gas from the sample space which maybe residual from the original cryogenic transfer or have built up during sample storage.

- The glass finger is isolated when the vacuum is within the 10⁻⁵ mbar range. The CO₂ sample is thawed out. A Baratron manometer is attached to this glass finger and allows an accurate pressure of the gas sample to be measured.

- The CO₂ is then frozen back into the sample bottle, and closed awaiting release into the mass spectrometer.

Normal mass spectrometer operating procedures are then followed for an analysis of the gas for ratio determination.

E.3 Calibration of the mass spectrometers

The mass spectrometers used for this research have been calibrated using a number of international standards. In addition to this the Prism and 602D have extended this to inter-calibrating with other laboratories. The calibration materials are listed below for each machine.

1) **VG Prism**

The prism at RHUL is calibrated using NBS19 (Calcium carbonate) and IAEA CO₂-9 (Barium carbonate). These are international δ¹³C standards.
The CO₂ reference gas used on a daily basis has been calibrated against the standards above and has been assigned a $\delta^{13}C_{\text{PDB}}$ value of $-37.5\%e$.

Laboratory intercalibration was undertaken with the European partners of the Atmospheric Monitoring and Isotope Laboratory. Four CO₂ gases were analysed for comparison. The stable isotope facility at RHUL produced values for these gases that fell within the range of all the values measured by the other laboratories (Levin et al., 1997). Quantities of two calibration gases, Heidi light ($-50.1\%e$) and ECN CO₂ standard ($-20.9\%e$) have remained at RHUL. Heidi light is analysed at the beginning of each day, when a new aliquot of CO₂ reference gas (CO₂-4) is loaded, and the ECN gas is run periodically to maintain precise calibration over the range of $\delta^{13}C$ values measured ($-21\%e$ to $-53\%e$).

2) **VG 602D**

Messr Griesheim supplied the H₂ reference gas used in this mass spectrometer. This is checked on days of analysis using Norwich Tap Water (NTW) reduced using Indiana Zinc. The data correction method is described in full in Chapter 6.

The VG602-D at UEA-SIL was internationally calibrated using 3 gases supplied as part of an exercise organised by Willi Brand. 36 laboratories participated in this test, the main aim of which was to determine the scale correction factors of mass spectrometers between SMOW and SLAP. The 3 gases measured were calculated to define a $\delta B_{\text{norm}}$ (Dennis, 1999, pers comm.) for each instrument. The mean of this combined isotopic measurement of the gases was $-408.0\%e$, the laboratory at UEA reported values of $-408.9\%e$. This was defined as a satisfactory calibration.

### E.4 Summary

The rigorous intercalibration of the mass spectrometers used to measure the gas products of the cryogenic extraction line gives confidence in the isotopic ratios measured and presented for this research.