

# Deuterium and Oxygen-18 on Surface Water and Groundwater



## Sampling and Submitting Samples

### *What to use*

The main factor that should be considered when sampling water for analysis of deuterium or oxygen-18 is to ensure that there is no potential for evaporation from the time the sample is collected until the time the sample is analysed. The best option is McArtney bottles, 30ml glass bottles with metal screw top lids with rubber inserts. These are a convenient size to run several replicates and tend to resist breaking during transport. Evaporation is minimal but, to reduce evaporation even further, samples should be stored and transported inverted. Any water loss is then in liquid form and does not result in changed isotope composition. Used McArtney bottles can be purchased at half new price from the CLW isotope laboratory by contacting the enquiry number. Plastic bottles may be used but please ensure when doing so that the lids are tightened, a volume of at least 100 mls is collected and that the sample is transported to the laboratory as soon as possible after collection to avoid evaporation of the sample.

### *Obtaining a representative sample*

The general consensus when sampling groundwater is that bores should be pumped out three or four times their holding volume to obtain a representative water sample. There remains some controversy whether this "rule of thumb" is appropriate, and to what extent the effect of pumping of water out of a bore has on the true in situ geochemical character of the aquifer after it has been essentially perturbed. For examples, pumping may generate a cone of drawdown which means we are taking a water sample at some depth other than that at which it is screened. In practice, we tend to sample a borehole after the pH or EC of waters being pumped has stabilized. This may take up to an hour in some instances. Ideally, run a plastic hose from the well head outlet to the bottom of the sampling bottles. Rinse the bottles at least twice then fill to overflow about three bottle volumes before sealing.

The process is considerably simpler when sampling surface water (for example from a river or lake). Simply rinse the bottle several times with water prior to filling the bottle from the required depth. Tighten the lid, store upside down and send to the laboratory. There is no need to filter the sample. Please do not add anything to the water sample. If something has been inadvertently added to the water, please advise the laboratory staff as it may cause difficulties with analysis. This particularly applies to mercuric chloride which is sometimes added to water samples to stop biological activity. Mercuric chloride will poison the platinum catalyst that is used when analyzing water for deuterium composition and replacing the catalyst is very costly.

## Analysis Methodology

### *Oxygen-18 Composition, (<sup>18</sup>O)*

The standard procedure for analysis of the Oxygen-18 composition of water is that described by Epstein and Mayeda (1953). This laboratory's modification involves equilibration of CO<sub>2</sub> with 1 ml of water in 6.5 ml 'Exetainers' Labco Ltd U.K. in a temperature controlled block held at 50 °C for 8 hours. The preparation and extraction of the CO<sub>2</sub> is automated using a 59 port water equilibration system, WES. This is attached to a GEO 20-20 dual inlet stable isotope gas ratio mass-spectrometer (PDZ Europa Ltd. U.K.).

Quality control is maintained by placing two tertiary laboratory water standards (deionized water that has been calibrated to the international primary standards VSMOW and VSLAP) at the beginning of each run, after every ten samples and at the end of the run.

Virtually all water samples, including water extracted from soil and plant material and water from reducing environments where hydrogen sulphide may be present can be analysed for <sup>18</sup>O using the WES method. However, for water samples with pH greater than 8-9, it is necessary to acidify the sample with a small amount of phosphoric acid prior to equilibration. Hence, please let the laboratory staff know that you are submitting alkaline waters.

Results are reported as per mille deviation from Vienna Standard Mean Ocean Water (‰ V-SMOW). Analytical uncertainty for naturally occurring waters is  $\pm 0.15$  ‰ (1 s.d). Water samples with artificially enriched levels of  $^{18}\text{O}$  are also measured using this method. The analytical uncertainty is typically double that for natural waters for most applications.

### ***Deuterium Composition, ( $^2\text{H}$ )***

The WES method is also used for analysis of the deuterium composition of water. The method is similar to  $^{18}\text{O}$  analysis via WES except that, for  $^2\text{H}$  analysis, hydrogen atoms from the water molecules are equilibrated with hydrogen gas rather than oxygen atoms equilibrating with oxygen in  $\text{CO}_2$ . A platinum catalyst is used to enhance the hydrogen equilibration process allowing complete equilibration within 1 hour.

As for  $^{18}\text{O}$  analyses, results are reported as per mille deviation from Vienna Standard Mean Ocean Water (‰ V-SMOW). Analytical uncertainty for naturally occurring waters is  $\pm 1.0$  ‰ (1 s.d) for both the WES and uranium reduction methods. Water samples with artificially enriched levels of  $^2\text{H}$  are also measured using this method. The analytical uncertainty is typically double that for natural waters for most applications.

### **References**

Epstein S. and Mayeda, T.K., 1953. Variations of the  $^{18}\text{O}/^{16}\text{O}$  ratio in natural waters. *Geochim. et Cosmochim. Acta*, 4: 213.

Europa Scientific Geo 20-20 (Europa, Crewe, Cheshire, UK) isotope ratio mass spectrometer.

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