SF_6 Sampling

The SF_6 mixing ratio in air and the solubility of this gas in water is low. A 15 cm^3 sample of air or unsaturated zone gas is needed for gas analysis. A minimum of a 1 liter of water is required to date groundwater with SF_6.

Bottle Ordering Information

A true 1-Liter sized, plastic safety coated, amber glass bottle with a polyseal cone lined cap is used.

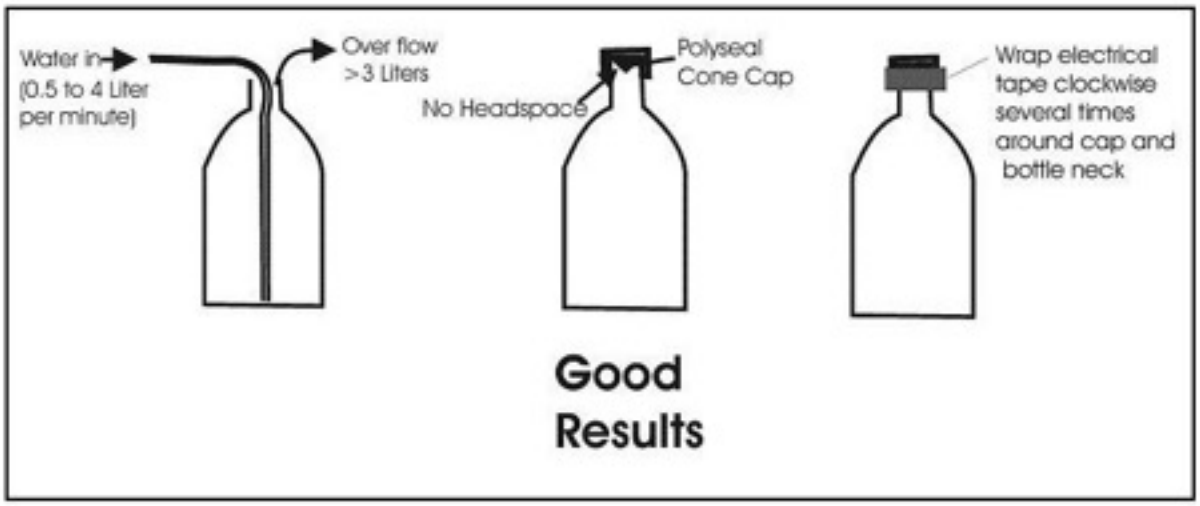
Additional Bottle Info and Pictures
You can order these 1-Liter plastic coated bottles from Qorpak Inc. at 1-800-922-7558. Catalog number GLA-00959 is for a case of 12 bottles or catalog number GLA-00958 is for a case of 30 bottles. Alternately, if coated bottles are unavailable, uncoated bottles can be used. Uncoated bottles do not ship as well as the plastic coated bottles. SF_6 bottles can be under pressure caused by the water warming up and expanding. Use of uncoated bottles is not recommended but will not cause any chemical or sampling problems. Breakage in shipping may be higher with uncoated bottles, pack them extra well for shipping. Uncoated bottles are available under Qorpak Inc stock number GLA-00903. The same cap fits either the coated or uncoated bottle.
The caps can be ordered from Brad-Pak Enterprises at 908-233-1234. Catalog number CPS-33E-B-PC-PS is a 33-430 size polyseal cone lined cap which fits the bottle.

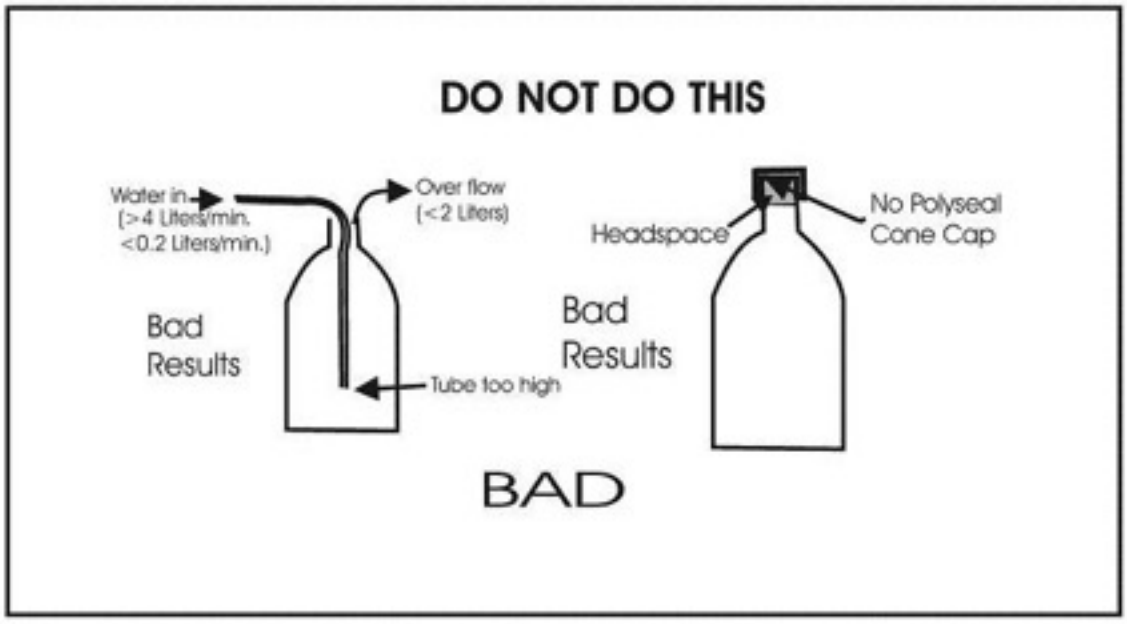
Field Collection of SF_6 Water Samples

The filling and capping procedure for SF_6 is done in the open atmosphere. Do not submerge the bottle and cap combination in a bucket for filling and capping. It is important that water **NOT** enter the area behind the cone seal in the cap. The area behind the cone seal allows the water to expand as it warms up without breaking the bottle.

1. Purge the well according to the USGS National Field Manual.
2. Place tubing from pump in the bottom of 1L bottle Additional Bottle Info and Pictures
3. Fill bottle and allow it to overflow from the neck. Allow three total liters of sample water to flow through the bottle with the tubing at the bottom of the bottle.
4. Slowly remove tubing from the bottle while water is still over flowing
5. Cap bottle tightly (**do not leave any headspace**) and tape cap in a clockwise direction with high quality electrical or similar tape.
6. Collect two bottles per site. Label each bottle with the environmental sample collection time and a sequence number in the order it was collected, 1-2.
7. Keep bottles in a cooler and not in the sun. If the bottles heat up excessively, the water will expand and may crack the bottle. Store samples at room temperature (23C) before shipping. Shipping on ice with other samples is acceptable but not necessary. Keep in mind that shipping in the summer will require ice to keep the bottles from warming excessively.

SF6 Sampling Prodedure





Gas Sampling Procedures

Gas samples can be collected in stainless steel cylinders that are equipped with inflow and outflow stainless-steel bellows valves. This design allows the cylinders to be flushed by the pumped air stream. The procedures that are used to collect gas samples in stainless steel cylinders are described in detail by Busenberg et al. (1991) and Thompson et al. (1985). The cylinders were filled in the laboratory with ultra-pure SF_6-free N_2. The N_2 in the cylinders is released prior to sampling by opening the outflow valves. The inflow valves are then opened to allow air flow through the cylinders for several minutes to purge the N_2. After the cylinders are completely flushed with air, the outflow valve is closed and pumping continues to pressurize the cylinder to about 2 atmospheres before closing the inflow valve.
Gas samples can also be collected in 100 mL borosilicate glass ampoules using procedures developed for sampling for CFCs (Busenberg and Plummer, 1992). The gas samples are heat-sealed in borosilicate glass ampoules with a torch.

Other Considerations

Shelf Life of SF_6 Samples
No changes in concentrations of SF_6 were observed after storage of 3 months.
Modification of SF_6 by Microbial Activity
No perceptible degradation of SF_6 was observed in highly reducing waters.
Unsaturated Zone Processes
When the unsaturated zone is relatively thin, the unsaturated-zone air composition tracks that of the troposphere (Oster et al., 1996). It is reasonable to assume unsaturated-zone SF_6 concentrations closely track tropospheric concentrations to unsaturated zone depths of less than 10 m (Weeks et al., 1982; Busenberg et al., 1993), in deeper unsaturated zones, there is a lag time for diffusive transport of SF_6 through the unsaturated zone. The time lag is largely a function of the

tracer diffusion coefficients, tracer solubility in water, and soil water content (Weeks et al., 1982; Cook and Solomon, 1995).

Dissolved Gases in Ground Water

It is recommended that some dissolved gas analyses be performed to determine the **recharge temperature** and the amount of *excess air* present in the ground waters. This can be done by submitting samples to the N_2 / Ar dissolved gas lab.

Recharge Temperature

Uncertainty in recharge temperature of 1 to 2°C introduces no significant error in the SF_6 model ground water age (±0.5 year) because of the rapid increase in the atmospheric mixing ratio of SF_6 of about 7 % per year (Geller et al., 1997).

Excess Air

Excess air is introduced into ground water when air bubbles dissolve during a rapid rise of the water table. The addition of excess air to ground water increases the SF_6 concentration of the groundwater above the air-water equilibrium concentration. If the presence of excess air is not considered in the calculation of an SF_6 model age, then the apparent age will be too young. If the excess air present in the ground water was not known, and was underestimated by one cm^3/kg of water at STP for typical U.S. ground waters, the age of the ground water will be under estimated by 1 to 2.5 years. In all cases, the error in the apparent date of recharge was higher for the waters that were recharged at the higher temperature. Excess air concentrations of 0 to about 2 cm^3/liter were found from N_2-Ar measurements on shallow groundwater recharged by aerial infiltration through sandy soils, however, concentrations as high as 10 cm^3/liter can be found in ground waters from some semi-arid regions.