



A rapid method for the measurement of sulfur hexafluoride (SF₆), trifluoromethyl sulfur pentafluoride (SF₅CF₃), and Halon 1211 (CF₂ClBr) in hydrologic tracer studies

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[1] A rapid headspace method for the simultaneous laboratory determination of intentionally introduced hydrologic tracers, sulfur hexafluoride (SF₆), trifluoromethyl sulfur pentafluoride (SF₅CF₃), Halon 1211 (CF₂ClBr), and other halocarbons in water and gases is described. The high sensitivity of the procedure allows for introduction of minimal tracer mass (a few grams) into hydrologic systems with a large dynamic range of analytical detection (dilutions to 1:10⁸). Analysis times by gas chromatography with electron capture detector are less than 1 min for SF₆; about 2 min for SF₆ and SF₅CF₃; and 4 min for SF₆, SF₅CF₃, and Halon 1211. Many samples can be rapidly collected, preserved in stoppered septum bottles, and analyzed at a later time in the laboratory. Examples are provided showing the effectiveness of the gas tracer test studies in varied hydrogeological settings.

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1. Introduction

[2] Tracers (chemicals, isotopes, fluorescent dyes, microspheres) have been extensively used in hydrologic studies to investigate water movement in aquifers, aquifer properties, transport in the unsaturated zone, and atmospheric exchange with surface water [Flury and Wai, 2003; Shapiro et al., 2008; Tobias et al., 2009; Ho et al., 2006; Clark et al., 1996]. Important tracer properties are (1) low toxicity, (2) commercial availability, (3) low cost, (4) chemical stability, (5) low retardation, (6) absent or low concentrations in the environment, (7) detection over a large concentration range, and (8) easy sampling and measurement procedures.

[3] Halocarbons, SF₆ and other tracers have been used to label the air in air rotary drilling in unsaturated zone and fractured rock studies [Davidson, 2002; Thorstenson et al., 1998]; to evaluate bacterial contamination in rotary mud drilling and rotary air drilling [McKinley and Colwell, 1996; Gronstal et al., 2009]; to determine partitioning in saturated, partially saturated columns with low and high organic carbon content [Wilson and Mackay, 1993, 1996]; to determine flow rates in an artificially recharged aquifer [Clark et al., 2004]; and in unsaturated zone studies [Vulava et al., 2002]; to determine diffusion rates in chalk above the water table [Darling et al., 1998]; to determine the tortuosity in the vadose zone [Tick et al., 2007]; to determine the properties of fractured rock aquifers



[Shapiro *et al.*, 2008]; to detect nonaqueous fluids in the saturated zone [Wilson and Mackay, 1995]; and to measure gas exchange in streams [Wanninkhof *et al.*, 1990]. In ocean studies, tracers are used to determine mixing rates, trace water masses, and to determine other processes in the oceans [Ho *et al.*, 2008; Watson and Ledwell, 2000; Watson *et al.*, 1991; Ledwell *et al.*, 1993; Ledwell and Watson, 1991]. SF₆ was used to measure transport, longitudinal dispersion and gas exchange in large tidal rivers [Clark *et al.*, 1994, 1996; Ho *et al.*, 2006, 2008] and small streams [Tobias *et al.*, 2007]; to study subsurface flow [Harden *et al.*, 2003]; to examine the geothermal potential of aquifers [Upstill-Goddard and Wilkins, 1995]; to identify recharge from a river [Gamlin *et al.*, 2001]; to trace groundwater discharge into streams [Cook *et al.*, 2006]; and discharge of septic tank effluent into the groundwater [Dillon *et al.*, 1999].

[4] This paper presents a new method for the rapid simultaneous determination and quantification of several gas tracers in water and gases. The high sensitivity of the procedure allows for introduction of minimal tracer mass in the field (a few grams) with a large dynamic range of detection, dilutions to less than 1:10⁸. Analytical times are less than 1 min for SF₆, about 2 min for SF₆ and SF₅CF₃, and about 4 min for SF₆, SF₅CF₃ and Halon 1211.

2. Properties of the Tracers

[5] Sulfur hexafluoride (SF₆) is a colorless, odorless, nonflammable, nontoxic, stable gas with excellent electrical insulating and arc-quenching properties. It is mainly used as an electrical insulator in high-voltage switches and transformers and as a blanket gas in the melting operations of magnesium metal production [Maiss and Brenninkmeijer, 1998; Busenberg and Plummer, 2000]. Industrial production of SF₆ began in 1953 with the introduction of SF₆-filled electrical switches [Maiss and Brenninkmeijer, 1998]. The preindustrial atmospheric mixing ratio of SF₆ was less than 0.05 parts per trillion by volume (pptv) [Busenberg and Plummer, 2000]. The 2008 North American atmospheric mixing ratio was about 7 pptv [Busenberg and Plummer, 2008]. Waters that contact crystalline rocks, or contact some carbonate rocks that have undergone diagenesis in contact with fluorine-bearing fluids in their geologic past can release high concentrations of terrigenous SF₆, and leave some ambiguity as to the source of SF₆

when detected. Because of its stability in anaerobic systems and extremely low detection limit (<1 pptv), SF₆ is a highly sensitive hydrologic tracer in systems in which terrigenous sources are not important.

[6] Trifluoromethyl sulfur pentafluoride (SF₅CF₃) has no known industrial uses, and the 2008 North American atmospheric mixing ratio was about 0.16 pptv [Busenberg and Plummer, 2008]. SF₅CF₃ has received considerable attention because it is the most effective greenhouse gas known with a warming potential of about 18000 times that of CO₂ [Sailer *et al.*, 2002]. The source of SF₅CF₃ in the atmosphere is still uncertain [Sturges *et al.*, 2000]. Preindustrial atmospheric concentrations were probably < 0.001 pptv and SF₅CF₃ can be detected to concentrations of < 0.01 pptv. There are no known terrigenous sources of SF₅CF₃, it is stable in anoxic waters [Busenberg and Plummer, 2008], and has been successfully used as a tracer in ocean studies [Ho *et al.*, 2008], and in a stream gas exchange study (this paper).

[7] Halon 1211 (CF₂ClBr) and Halon 1301 (CF₃Br) are entirely of anthropogenic origin, are electrically nonconducting, volatile, fire extinguishing agents, and have low toxicity, are chemically stable, and do not leave a residue upon evaporation [Butler, 1998]. Halon fire extinguishers are used in closed areas such as aircraft and boats. The USEPA recognizes that halons are very effective extinguishing agents, and the agency continues to allow the use of recycled halons despite their ozone depleting potential [Daniel *et al.*, 1999; Montzka *et al.*, 2003]. The atmospheric mixing ratios are about 4.3 and 3.2 pptv for Halon 1211 and Halon 1301, respectively (<http://agage.eas.gatech.edu/data.htm>) [Reeves *et al.*, 2005]. Halon 1211 can be detected to concentrations of about 0.2 pptv. The atmospheric lifetimes of Halon 1211 and 1301 are 16 and 65 years, respectively [Forster *et al.*, 2007]. Halon 1211 was detectable in unsaturated zone gases 15 years after it was introduced in a well at Yucca Mountain, Nevada [Thorstenson *et al.*, 1998] and in groundwater 5 years after it was introduced in a fractured rock aquifer in Virginia (this paper). Some important properties of these tracers are summarized in Table 1.

[8] Henry's law solubility is used to reconstruct water concentrations from analyses of tracers in gas headspaces in septum bottles that have been equilibrated at laboratory temperatures. The temperature dependence of Henry's law solubility of



Table 1. Selected Properties of SF₆, SF₅CF₃, Halon 1211, and Halon 1301^a

Compound	Toxicity	Commercial Availability	Chemical Stability	Retardation in Aquifer	Atmospheric Concentration ^b	Detection Limits ^c (ppt)	Analysis Minutes
SF ₆	Very low	Yes	Stable	Very low	7.0	0.5	<1
SF ₅ CF ₃	Very low	Yes	Stable	Low	0.16	0.01	2
Halon 1211	Low	Yes recycled ^d	Unknown ^e	Unknown ^f	4.3	1	4
Halon 1301	Low	Yes recycled ^d	Unknown ^g	Unknown ^f	3.2	5	3

^aSee text for details.

^bThe 2008 atmospheric mixing ratios in parts per trillion by volume.

^cDetection limits in the gas phase are in parts per trillion but depend on the volume of the serum bottle, the volume of water sample, and the volume of headspace gas injected into the gas chromatograph.

^dRecycled halons are commercially available.

^eHalon 1211 atmospheric lifetime is 16 years but was found to be stable in the unsaturated zone and groundwater for many years.

^fThe retardations of halons have not been determined but are likely to be low.

^gHalon 1301 has an atmospheric lifetime of 65 years and is more stable than Halon 1211.

the tracers in pure water is described by the Clark-Glew-Weiss equation

$$\ln K = A + B \times \left(\frac{100}{T}\right) + C \times \ln\left(\frac{100}{T}\right) \quad (1)$$

where A , B and C are constants given in Table 2. The temperature T is in degrees Kelvin. The temperature dependence is plotted in Figure 1. The molar solubility range of the tracers in water spans more than four orders of magnitude. The Henry's law solubility of SF₆, SF₅CF₃, and CF₂ClBr and CF₃Br are from Bullister *et al.* [2002], Busenberg and Plummer [2008], and Deeds [2008], respectively.

3. Sampling and Analytical Procedure

[9] Water samples were collected in Wheaton "125" mL serum glass bottles (actual volumes are 159.5 ± 0.5 mL). The bottles were sealed with Bellco Glass 20 mm rubber stoppers. The oxygen in the bottles was reduced by purging with N₂ gas (procedure shown in Figure 2a). High concentrations of O₂ can interfere with the determination of SF₆. Several bottles can be prepared simultaneously. After the majority of the oxygen was removed, the needle inlet of nitrogen was removed

and then the second needle was removed after the over pressure was relieved (nitrogen stopped bubbling out of the serum bottle). The serum bottles were weighed and numbered with a permanent marker. The serum bottles can be stored several weeks before use. The sample can be injected into the bottle using a needle as shown in Figure 2b. The sample-filled bottles are weighed and the volume of the water was determined by difference. The headspace gas was allowed to equilibrate with the water sample for several days at constant temperature. The headspace was then sampled as shown in Figure 2c for analysis. No discernible loss of SF₆ and SF₅CF₃ was observed during storage for a period of 1 month [Busenberg and Plummer, 2008], similar results were obtained with halon (this study).

[10] Two sources of N₂ gas were present in the serum bottle, the N₂ that was present in the bottle before the water sample was injected, and the dissolved N₂ in the water sample. The moles of gas in the empty serum bottle are equal to:

$$n_1 = \frac{P_1 V_1}{RT_1} \quad (2)$$

where n_1 is the moles of N₂, P_1 is the room barometric pressure (atm.), V_1 is the volume of the

Table 2. Henry's Law Solubility Fit Parameters of the Clark-Glew-Weiss Equation for Sulfur Hexafluoride (SF₆), Trifluoromethyl Sulfurpentafluoride (SF₅CF₃), Halon 1211 (CF₂ClBr), and Halon 1301 (CF₃Br) in Pure Water^a

Compound	Volumetric (mol L ⁻¹ atm ⁻¹)			Gravimetric (mol kg ⁻¹ atm ⁻¹)		
	A	B	C	A	B	C
SF ₆	-96.5975	139.883	37.8193	-98.7264	142.803	38.8746
SF ₅ CF ₃	-12.8108	23.9976	-3.9715	-14.9316	26.9057	-2.9203
Halon 1211 (CF ₂ ClBr)	-92.9683	140.1702	36.3776	-95.0891	143.0783	37.4288
Halon 1301 (CF ₃ Br)	-166.195	248.842	71.0524	-168.3155	251.75	72.1036

^aSources are as follows: (SF₆), [Bullister *et al.*, 2002]; trifluoromethyl sulfurpentafluoride (SF₅CF₃), Busenberg and Plummer [2008]; Halon 1211 (CF₂ClBr), Deeds [2008]; Halon 1301 (CF₃Br), [Deeds, 2008].

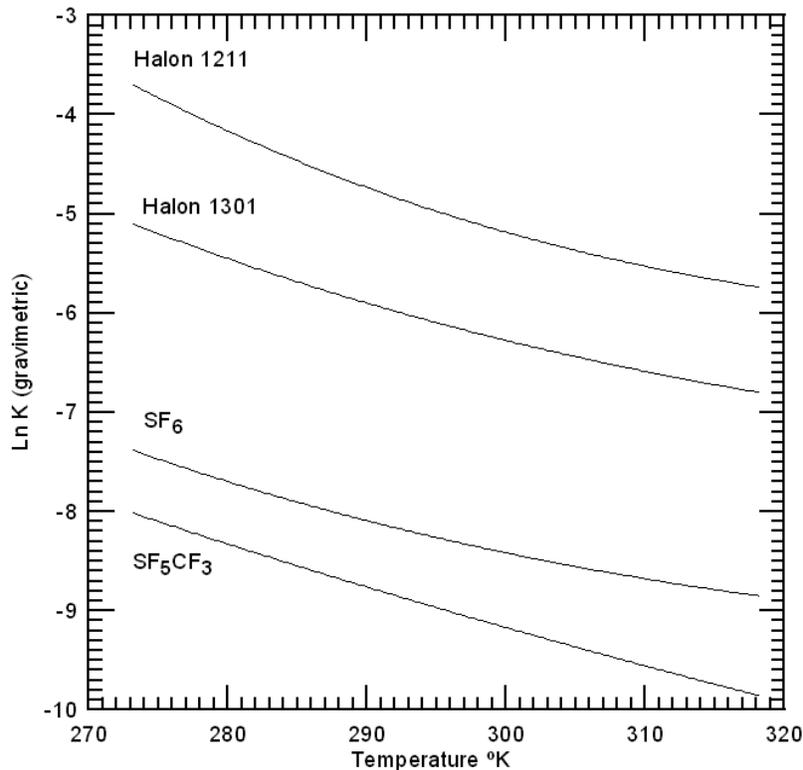


Figure 1. Ln K of sulfur hexafluoride (SF_6) [Bullister *et al.*, 2002], trifluoromethyl sulfurpentafluoride (SF_5CF_3) [Busenberg and Plummer, 2008], Halon 1211 (CF_2ClBr) [Deeds, 2008], and Halon 1301 (CF_3Br) [Deeds, 2008] in pure water as a function of temperature.

serum bottle (L), T_1 is the room temperature ($^{\circ}\text{K}$), and R is the ideal gas constant.

[11] The moles of N_2 in the water (n_2) can be measured or can be calculated if the water was in equilibrium with the atmosphere using the expression:

$$n_2 = K_2(P_2 - P_{2,\text{H}_2\text{O}})x_2v_2 \quad (3)$$

where K_2 is the Henry's law constant, P_2 is the atmospheric pressure at the sampling site (atm.), $P_{2,\text{H}_2\text{O}}$ is vapor pressure of water (atm.), x_2 is the mole fraction of N_2 in the atmosphere, and $v_{\text{H}_2\text{O},\text{bottle}}$ is the volume of sample (L).

[12] The moles of N_2 present in the water sample were about 0.1–0.2% of the total moles of N_2 in the bottle. The amount depended on the volume of the serum bottle, and concentration of N_2 , and volume of the water sample. The N_2 introduced by the water with the 159.5 mL serum bottles was less than the analytical precision of about 1%. The pressure contribution of N_2 and all the other dissolved gases was significantly smaller than the analytical uncertainty and can be calculated.

[13] In most cases, dry gas pressure of the headspace (P_3) can be closely approximated by the equation:

$$P_3 \approx \frac{V_1 P_1 T_3}{T_1 (V_1 - v_{\text{H}_2\text{O},\text{bottle}})}, \quad (4)$$

where the total pressure in the headspace is equal to $P_3 + P_{3,\text{H}_2\text{O}}$, and T_3 is the room temperature. From the gas law, the moles of the tracer in the serum bottle headspace ($n_{i,\text{headspace}}$) equals $(P_3 p_{i,\text{meas}} V_{\text{headspace}})/(T_3 R)$ where $p_{i,\text{meas}}$ is the

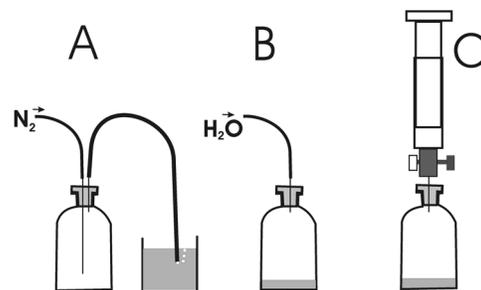


Figure 2. Procedures used (a) to prepare the serum bottles, (b) to inject the sample, and (c) to sample the headspace gases. See text for details.

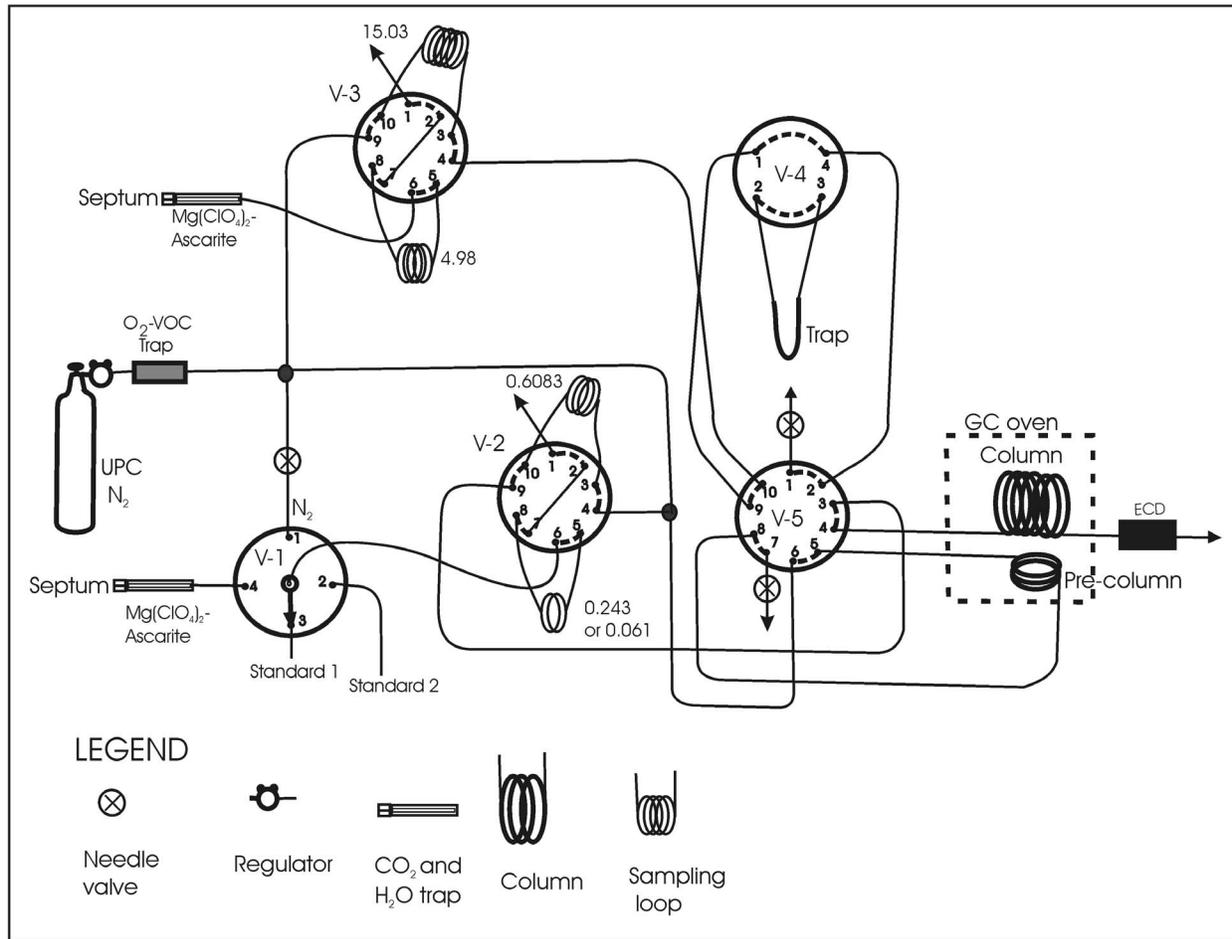


Figure 3. The analytical system used to measure the concentration of the tracers in the headspace gas. Small volumes are directly injected through V-1 into the gas chromatograph, and large volumes of gas are injected through V-3, are trapped, and are then injected into the gas chromatograph. The volumes of the sampling loops in cm³ are shown in the diagram.

measured tracer partial pressure and $(P_3 \times p_{i,meas.})$ is the partial pressure of the tracer in the headspace in atm. From Henry's law, the water concentration in the serum bottle in moles/liter ($C_{i,bottle}$) is equal to $P_3 p_{i,meas.} K_{i,lab.}$, where K in Henry's law constant. The concentration of the tracer in aquifer in mol/L then equals

$$C_{i,aquifer} = (C_{i,bottle} V_{H_2O,bottle} + n_{i,headspace}) / V_{H_2O,bottle} \quad (5)$$

The apparatus used to measure the tracers is similar to the one described by Busenberg and Plummer [2008] and is shown in Figure 3. The apparatus consists of two different systems, the first directly measures the gas injected and consists of valves V-1, V-2 and V-5; the second traps the gas tracers in a cooled trap; then releases the tracers when the trap is heated and consists of valves V-3, V-4 and V-5.

[14] The first system can directly inject the gas samples or can trap the tracers in the samples when V-5 is turned and V-4 is turned to open the trap that is cooled to -70°C . The trapping removes the oxygen that may be present in the headspace gas but increases the elution time of the tracers.

[15] With the exception of the background samples, the rest of the samples were injected directly into the gas chromatograph without any further processing. The standards and blank are injected into the analytical system through selector valve V-1. The headspace gas samples were injected through a septum and a trap with 0.5 cm inner diameter glass tube filled with 6 cm of $\text{Mg}(\text{ClO}_4)_2$, 6 cm of Ascarite® (NaOH on an inert mineral matrix) followed by 6 cm of $\text{Mg}(\text{ClO}_4)_2$. The sorbents were separated with glass wool. The trap removes the water vapor and CO_2 from the headspace gas

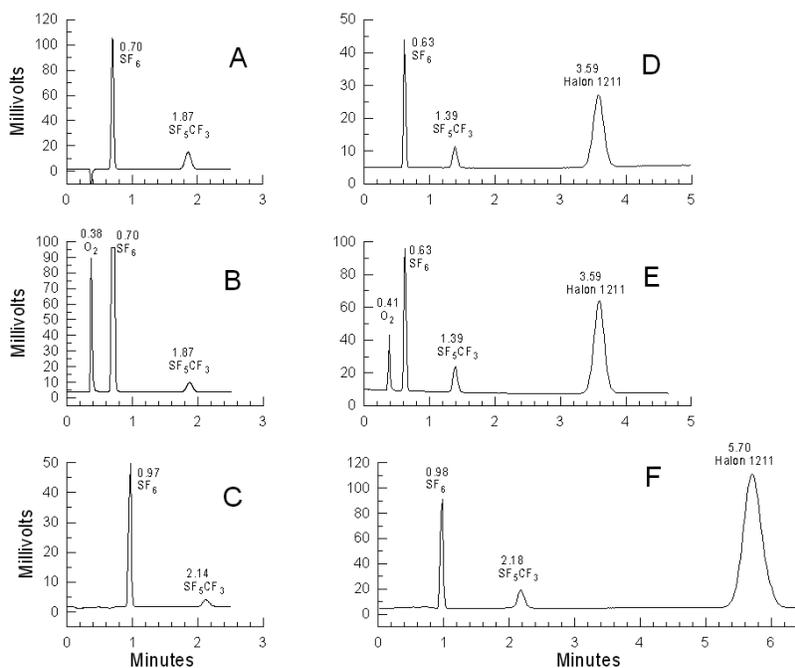


Figure 4. Chromatograms of samples and standards analyzed by the analytical system. (a and d) The chromatograms of standards. (b and e) Chromatograms of headspace gas directly injected through the column into the GC. Note the presence of some oxygen. (c and f) Chromatograms of headspace gas that was trapped and then injected through the precolumn and the column into the GC. The trapping of the tracers removes the oxygen present but slightly increases the retention times.

samples. Alternatively, a Nafion® trap can be used to remove the water vapor, however, this type of trap does not remove the CO₂.

[16] The background samples, air samples (high in oxygen) with very low tracer concentrations were injected through the moisture-CO₂ trap into the loops of V-3. After the trap on V-4 is opened, V-3 was turned to inject the samples into the 15 cm and 0.32 cm diameter stainless steel trap filled with 60–80 mesh Porapak T® and cooled to –70°C with an ethanol–dry ice mixture. The tracers from more than a single injection of the sample can be trapped. The trap was then closed, heated to 95°C and valve V-5 was turned. When V-4 was turned and opened, the tracers were released, passed through the 30 cm and 0.32 cm diameter stainless steel precolumn filled with 5 Å molecular sieve, then through a 2.4 m and 0.32 cm diameter stainless steel column filled with 60–80 mesh CarboPak B coated with 1% SP-1000 (Supelco column 1–2543-U). The chromatograms shown in Figure 4 were obtained at a gas chromatograph oven temperature of 120°C. The N₂ carrier flow rate was 30 mL min⁻¹ and the electron capture detector temperature was 300°C. After the run, valve V-5 was switched to the position shown in Figure 3, flushing to the vent the

highly retentive compounds in the precolumn and significantly reducing the analytical time.

4. Case Studies

[17] A variety of tracer studies were conducted by the U.S. Geological Survey and the samples analyzed at the Groundwater Dating Laboratory in Reston, Virginia. A few case studies that highlight the effectiveness of the SF₆ and other tracers used are described below.

4.1. Testing for Leakage Through a Semiconfining Layer, Albany, Georgia

[18] An SF₆ and dye tracer test was conducted near Albany, Georgia to study the potential leakage from a shallow contaminated water table aquifer into a deeper confined aquifer. The two aquifers were separated by an “impermeable” aquitard. A shallow well (9.2 m depth) was completed in the unconfined aquifer and separated by a distance of 152 m from a 61 m deep well completed in the underlying confined aquifer.

[19] In this test, rhodamine WT was added to 416 L of groundwater and then the water was saturated

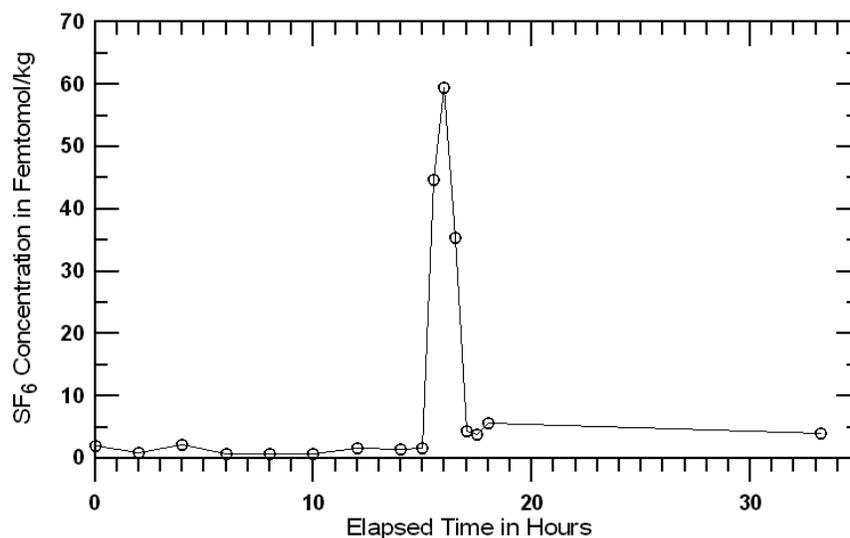


Figure 5. Concentration of SF₆ in the samples obtained from the deep well as a function of elapsed time from the addition of the tracer in the shallow water table aquifer well.

with SF₆. The water was poured into the shallow well. The deep well was pumped and the groundwater was sampled. No rhodamine WT was detected in the samples collected from the deep well, however, the SF₆ spike was observed beginning at 15.5 h after the tracers were added to the shallow well. The SF₆ concentration remained above background of 1.2 fmol/kg 34 h after the start of the test. The results of the test are shown in Figure 5 and indicate potential leakage from a shallow contaminated water table aquifer into a deeper aquifer.

4.2. Injection of SF₆ Into Karst in Southeast Florida

[20] Shapiro *et al.* [2008] used SF₆ to evaluate the potential of pathogen migration in the karst Biscayne limestone aquifer of southeastern Florida. The water was injected into the aquifer from three tanks. One 189 L tank contained dissolved SF₆ and Halon 1211, a second 189 L tank contained deuterium oxide and microspheres, and a third larger tank (379 L) contained formation water. The waters from the two smaller tanks were mixed and injected into a 3.5 m packed off interval (elevation -7.6 to -11.1 m) of the well over a period of about 20 min and was followed by the injection of a 379 L volume of tracer-free groundwater [Shapiro *et al.*, 2008]. Water samples were collected from a 1.22 m diameter well located approximately 97m from the injection well; the production interval was 10.3 m (elevation -10.7 to -21m). The first detection of SF₆ occurred in about 5.5 h with the

maximum peak concentration at 8.25 h. The breakthrough SF₆ curve showed an elongated tail that was detectable 6 days after injection when sampling was stopped. The extended retention of SF₆ in this high-transmissivity karst-carbonate aquifer was attributed to a combination of chemical diffusion and slow advection. Plots of the SF₆ concentrations as a function of elapsed time as well as detailed description of the results of this study are given by Shapiro *et al.* [2008]. The Halon 1211 and deuterium oxide results were unsatisfactory because the concentrations injected were too low to be used in this study [Shapiro *et al.*, 2008]. The recovery of microspheres and the potential of transport of *Cryptosporidium parvum* oocysts in the Biscayne aquifer was examined by Harvey *et al.* [2008].

4.3. SF₆ Gas Exchange From Surface Water

[21] SF₆ was added to stream water to study time-variable gas transfer between stream water and air [Tobias *et al.*, 2009]. A 36 h continuous injection of a small constant flux of water saturated with SF₆ was used with concurrent collection of other dissolved gases to evaluate dissolved gas mass balance in the stream. This provided a record of the changes in gas transfer velocity that was contemporaneous with the sampling of nonconservative dissolved gases. In a single diel period there was a 30 percent variation in the gas transfer velocity in a second-order stream. The changes were attributed to combined effects of temperature and wind velocity [Tobias *et al.*, 2009]. Time variable gas transfer velocities derived from these measure-

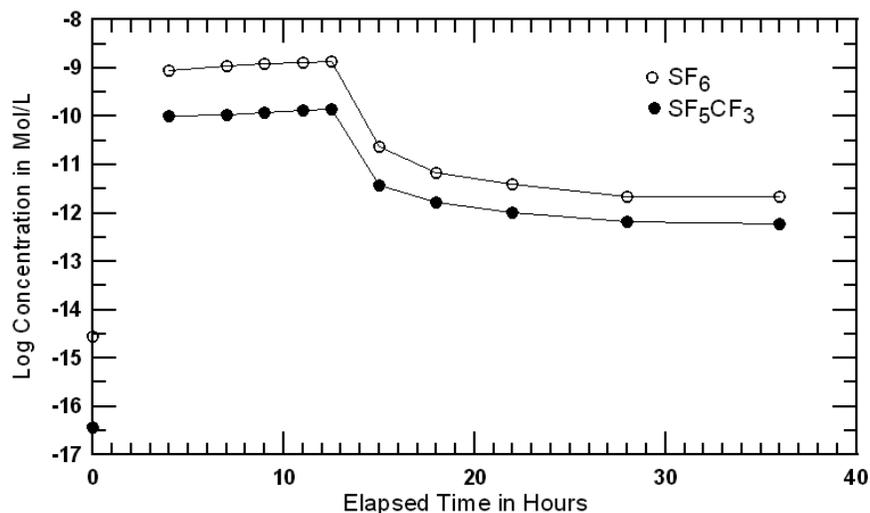


Figure 6. Concentrations of SF₆ and SF₅CF₃ in samples collected from one of five sampling sites in a small stream. The concentrations before during and after the tracer addition period are shown. The addition of tracers began at 0 elapsed time.

ments were used with other chemical and isotopic tracers to model biochemical processes in the stream including photosynthesis, respiration, and denitrification [Tobias *et al.*, 2007; Böhlke *et al.*, 2009]. In another study, both SF₆ and SF₅CF₃ were used. Figure 6 shows preliminary results at one of 5 locations of sample collection (C. R. Tobias *et al.*, unpublished data, 2009). The background concentrations were about 2.8×10^{-15} and 3.4×10^{-17} moles per kg of SF₆ and SF₅CF₃, respectively. The slightly increasing straight line segments represent a period of constant continual injection of the tracers that was followed by decreasing concentrations of the tracers after the injection stopped.

4.4. Tracers in Drilling Mud

[22] Halon 1211 tracer and fluorescent microspheres were added to drilling mud to evaluate fluid and microbial contamination of core samples obtained from the well drilled into the Chesapeake Bay Impact structure [Gronstal *et al.*, 2009]. A one percent gas mixture of Halon 1211 in nitrogen was dissolved under pressure in the drilling mud to produce a concentration of about 1 ppm Halon 1211. A one percent fraction of this fluid mixture is 1000 times above the detection limit of the analytical method (which allows for a large range of detection and dilution). The returning drilling mud was sampled to verify the presence of Halon 1211. The exterior of the cores as well as the center of the cores were rapidly sampled to minimize the loss of halon to the atmosphere. Samples taken from the

cores were placed in preweighed serum bottles and sealed with gas tight stoppers. The headspace gas was analyzed by the procedures described above for the presence of Halon 1211. For these analyses, the oven temperature was increased from 120°C to 170°C to reduce the retention time of Halon 1211 from 4 to 1.7 min. The tracer data indicated that the samples used for detailed studies were not contaminated with bacteria present in the mud or mud fluids [Gronstal *et al.*, 2009].

4.5. Tracers of Drilling Air in Air Rotary Drilling

[23] Numerous wells were completed in the Piedmont Physiographic Province of North Carolina and Virginia using air rotary drilling. The air was tagged with Halon 1211. The addition of tracers during drilling was used to identify contamination of the groundwater with air in future sampling. Air-contaminated samples are difficult to date with the CFC, SF₆ and ³He/³H methods. The Halon 1211 introduced during drilling was present in the groundwater 5 years after the well was completed in fractured rocks in Loudoun County, Virginia. Contamination with drilling fluids and air can be a persistent problem in some wells that have not or cannot be properly purged [Plummer *et al.*, 2004]. Halon 1211 was detectable above background levels of <1 pptv in unsaturated zone gases 15 years after it was introduced in a well at Yucca Mountain, Nevada [Thorstenson *et al.*, 1998]. The presence of Halon 1211 in air and groundwater do not



interfere with the analysis of SF₆ and CFCs, but age interpretation is probably invalid.

5. Conclusions

[24] The analytical procedure described in this paper can be used to rapidly and simultaneously measure numerous halogenated compounds at very low concentrations in hydrologic tracer studies. Analytical time is less than 1 min for SF₆, and about 4 min with three tracers. A large number of samples can be collected for analysis using a headspace method, a procedure that has been successfully used for the past 15 years by the U.S. Geological Survey in a variety of studies. The large dynamic analytical range allows the use of small amounts of tracers of low toxicity that are commercially available at low cost and that are chemically stable in the aquifers.

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[25] The manuscript was improved by the reviews of David L. Nelms, Brian G. Katz, John Karl Böhlke, and Michael W. Doughten. The use of brand names in this report is for identification purposes and does not imply endorsement by the U.S. Geological Survey.

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