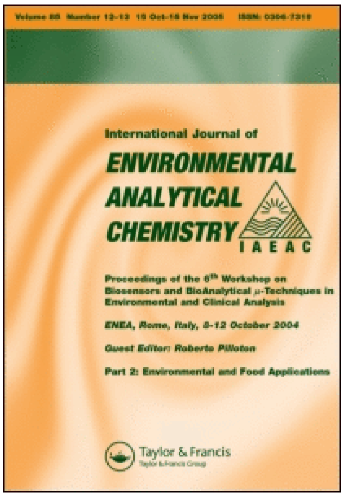

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DISSOLVED OXYGEN AND METHANE IN WATER BY A GC HEADSPACE EQUILIBRATION TECHNIQUE

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An analytical procedure is described for the determination of dissolved oxygen and methane in groundwater samples. The method consists of generating a helium gas headspace in a water filled bottle, and analysis of the headspace by gas chromatography. Other permanent gases such as nitrogen, and volatile aliphatic hydrocarbons such as ethane, propane, and butane could also be analyzed. BTX analyses could also be done on the sample. Detection limit for oxygen was 0.1 mg/l and 0.002 mg/l for methane. Good agreement was shown between Winkler titration and the GC-Headspace Equilibration Technique for oxygen analyses by a linear regression coefficient, $R^2=0.998$. Oxygen was greatly depleted in some field samples when they were stored for 30 days at 4°C without hydrochloric acid preservation.

KEY WORDS: Dissolved oxygen, GC, headspace, Henry's law, water, BTX.

INTRODUCTION

The concentration of dissolved oxygen, methane and aromatic hydrocarbons (BTXs) are important in evaluating biological activity with aquifers contaminated by petroleum fuels. Analytical methods are available for all three parameters, but each requires tedious separate sampling and analysis protocol.

The two methods most widely used for dissolved oxygen determination in water are Winkler titration and direct probe readings.[1] Both are reliable, but they require appreciable volumes of sample. Some gas chromatography methods for determining dissolved gases from solution are by inert gas purging,[2] *in situ* buried diffusion cells or probes,[3] direct injection into a heated column then separation from the vaporized liquid[4,5] or equilibrium of a solution in a closed bottle with an inert gas headspace.[6] The last approach has advantages of simplicity, reliability, and adaptability to routine analyses of samples.

Henry's law states that the equilibrium value of the mole fraction of gas dissolved in a liquid is directly proportional to the partial pressure of the gas above the liquid surface, or $x_g = p_g/H$, where p_g = equilibrium partial pressure of gas, x_g = mole fraction of dissolved gas, H = Henry's law constant.[7] Henry's law is applicable at low concentrations and low partial pressures of a gas at or below one atmosphere pressure. Solubility data can be obtained from technical handbooks relating H values to temperature.[8,9]

Described is a technique for the analysis of dissolved oxygen and methane in water. The method is also applicable to nitrogen and other volatile aliphatic hydrocarbons. The aliquot of water removed during headpsace generation can be used for volatile organics analyses by EPA methods 601 or 602.[10]

EXPERIMENTAL

Sample Collection and Preparation

Water samples collected in the field or prepared in the lab were placed into 50 ml borosilicate glass Hypo-Vials (Pierce, Rockford, IL) and capped with aluminium seals and Teflon faced butyl rubber septa (Wheaton Scientific, Millville, NJ). Actual bottle volume was near 62 ml. Total volume for each bottle was measured by refilling with water and measuring the quantity. Water samples were added to the bottles down the side to prevent agitation and subsequent oxygen contamination. Also, care was taken to make sure that no air bubbles were entrapped in the sample. Initially, field samples were stored at 4 °C and analyzed by GC within four to eleven days after collection. In a later sample set, 0.15 ml of 1:1 of water:12 M HCl was added as a preservative. Winkler titrations were fixed and analyzed within 10 minutes of collection to conform to EPA guidelines.[10]

Headspace generation was done by placing the sample bottle upside down in a three finger clamp (Figure 1). A 20 gauge needle on a 10 ml Luerlock glass syringe, set for dead volume, was inserted into the sample by penetrating the septum about one centimeter. An 8 cm 22 gauge needle attached to Teflon tubing via a Mininert syringe valve was then inserted through the septa to the top of the water. A flow of five milliliters per minute of high purity helium was passed through the syringe valve. After six milliliters of water was forced from the bottle into the syringe, both needles were removed. The displaced water could then be used for BTX analysis. The sample bottles, which contained ten percent by volume helium headspace, were shaken five minutes at 1400 rpm on a rotary shaker (Tekmar VRX Vibrax, Thomas Scientific, Swedesboro, NJ) to allow gases to equilibrate between the liquid and gas phases. Samples for headspace analysis of both oxygen and methane were taken immediately after the five minute rotary shaking period.

Headspace Analysis

Oxygen GC Parameters—100 μl of the headspace was withdrawn with a 500 μl

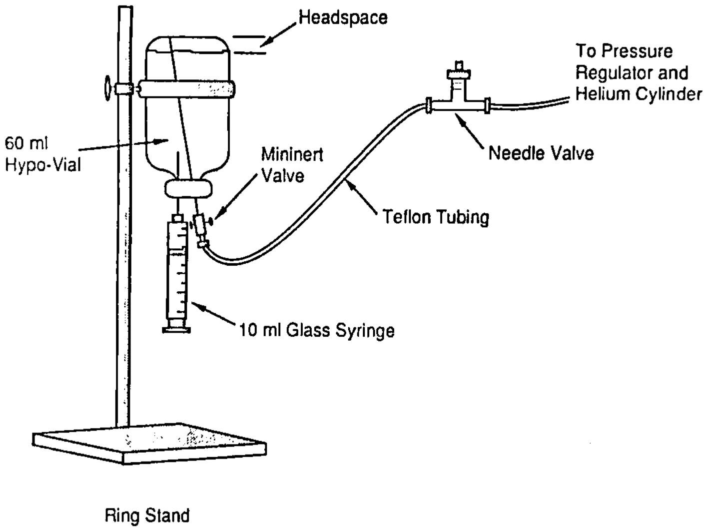

Figure 1 Headspace generation set-up for the headspace equilibration technique.

gas-tight syringe (Precision Scientific, Baton Rouge, LA), and injected into a Varian Vista 6000 GC for oxygen analysis. The column used was 6′ × 1/8″ stainless steel, 60/80 molecular sieve 5A (Supelco, Inc., Bellefonte, PA). Two columns were used with one each for the analytical and reference side. Carrier gas was high purity helium at 20 mL/min. The column oven was set at 50 °C, injector at 120 °, TCD at 120 °, and TCD filament at 140 °. The TCD Attenuation = 1 and Range = 0.5 mV. Oxygen and argon chromatogram peaks were not resolved by the molecular sieve column at 50 °C oven temperature. Peak retention times in minutes were 0.98 for oxygen and 2.17 for nitrogen. Ambient air was used for calibration. It was assumed to be 21 % oxygen. Detection limit for oxygen was 0.1 mg O_2/liter water.

Background Interference—Air equivalent to the syringe needle volume was unavoidably introduced into the GC during injection of the 100 μl headspace sample. Repeated analyses determined that about 2 μl oxygen + argon, which coelute, was introduced with each sample injection. This background may be reduced considerably by pumping the syringe several times into the 6 ml headspace. Confirmation of argon's contribution to the oxygen peak area was done by use of an activated charcoal packed postcolumn. This removed oxygen and left only argon to be measured. During routine analyses, argon was not determined for each sample since reconditioning of the charcoal + molesieve columns required a lengthy time period at elevated temperature. The background correction value for argon was determined by analyzing some water samples containing a slight excess of sodium sulfite, which consumed all the dissolved oxygen. Magnitude of the argon peak is shown in the example calculation.

Calculations—Pressure was assumed to be one atmosphere. Other variables needed for concentration are temperature and the actual volume of each sample bottle. Water samples were allowed to reach room temperature before generation of headspace and subsequent analysis. Bottle volumes were determined by emptying refilled bottles into a graduated cylinder and recording the volume.

Example calculation from chromatogram peak areas obtained by analyzing air-saturated water at 20 °C.

	Peak area
100 μl calibration standard, 21 % oxygen	$126450 = A$
Air-saturated water, oxygen	$32759 = B$
2 μl syringe needle contribution	$2360 = C$
Background, argon	$3649 = D$

It is assumed that argon partitions the same as oxygen. Then response due to argon in ambient air is 3649/126450 or 2.88 %. Then $E = 1 - 0.0288 = 0.971$.

$$\text{Partial pressure of oxygen, } Pg = \frac{(B - C) \times E}{A - D} \times 0.21 = 0.050.$$

$$\text{Equilibrium mole fraction of dissolved oxygen, } x_g = \frac{Pg}{H}$$

or

$$\frac{0.050}{4.01 \times 10^4} = 1.247 \times 10^{-6} \text{ moles } O_2.$$

Let

$$n_g = \text{moles gas and } n_w = \text{moles water.}$$

Then

$$x_g = n_g/(n_g + n_w) \quad \text{and} \quad n_g = x_g(n_g + n_w).$$

Since one liter of water is 55.51 g-moles,

$$n_g = (n_g + 55.5)(1.247 \times 10^{-6}) \text{ and since } n_g\ (1.247 \times 10^{-6}) \ll n_g,$$

$$n_g \approx 55.5\ (1.247 \times 10^{-6}) \text{ or } 6.92 \times 10^{-5} \text{ moles/liter oxygen.}$$

Saturation concentration of oxygen,

$$C = \frac{(n_g)(32\ \text{gm})(100\ \text{mg})}{(\text{mole } O_2)(g)}$$

$$= (6.92 \times 10^{-5})(32)(1000) = 2.21 \text{ mg } O_2\text{/liter headspace oxygen.}$$

$$\text{Density} = 22.4\,\text{liter/mole} \times \frac{293\,°\text{K}}{273\,°\text{K}} = 24.04\ \text{liter at } 20\,°\text{C}$$

or

$$\frac{32\,\text{gm/mole}}{24.04\,\text{liter/mole}} = 1.33\,\text{gm O}_2\text{/liter.}$$

Bottle volume = 62.5 ml and headspace volume = 6 ml.

So, 6 × 0.050 = 0.300 ml oxygen and liquid phase oxygen is

$$\frac{0.300\,\text{ml O}_2}{0.0565\,\text{liter H}_2\text{O}} \times 1.33 = 7.06\,\text{mg O}_2\text{/liter.}$$

Then liquid phase oxygen and headspace oxygen = 7.06 + 2.21 = 9.27 mg O_2/liter. Standard tables list 20 °C air-saturated water to contain 9.2 mg O_2/liter. This is in good agreement with the value of 9.27 mg O_2/liter shown above. Data listed in Table 2 was obtained from four sets of samples. New calibration units A and D were determined for each set to obtain a computer entry constant of $(E)(0.21)/(A-D)$. Partial pressure of oxygen Pg, for each sample in a set then was determined from $(B-C)$ × the constant.

Methane

GC Parameters—Immediately after oxygen analysis was completed on a sample, analysis for methane was done on the headspace by withdrawing another 100 μl and injecting into a Varian 3300 GC equipped with an FID. Column used was 5′ × 1/8″ stainless steel tubing containing Porapak N 80/100. Carrier gas was high purity helium at 25 mL/minute flow. Hydrogen and air flow for the detector was 30 and 300 mL/minute respectively. The column oven was 160 °C. The injector and detector were both 190 °C. Under these GC conditions, the following retention times in minutes were obtained using a 0.1% "Scotty" hydrocarbon gas standard (Scott Specialty Gases, Plumsteadville, PA): 0.31 for methane, 0.40 for ethane, 0.56 for propane, 0.92 for *n*-butane, 1.64 for pentane, and 3.10 for hexane. Detection limit for methane was 0.002 mg CH_4 per liter water. Since typical air is essentially methane free and good resolution of GC peaks was obtained, no correction was needed.

RESULTS AND DISCUSSION

Water samples prepared in the laboratory or collected at a Michigan field site were analyzed by our described procedure with emphasis placed on dissolved oxygen. Table 1 shows analytical data on a water sample that was saturated by purging with air ("oxygen") and natural gas ("methane").

Some chromatograms obtained for the analysis of water samples are shown in Figure 2. Table 2 lists the analytical results obtained from 26 water samples. The

Table 1 Replicate analyses of saturated water

	Oxygen	*Methane*
Expected	9.2	23.2
Rep A	9.17	19.2
Rep B	8.98	19.2
Rep C	9.22	19.7
Rep D	9.62	18.5
$\bar{x}$	9.25	19.16
Agreement ($\bar{X}$/Expected) × 100	100.5%	83%

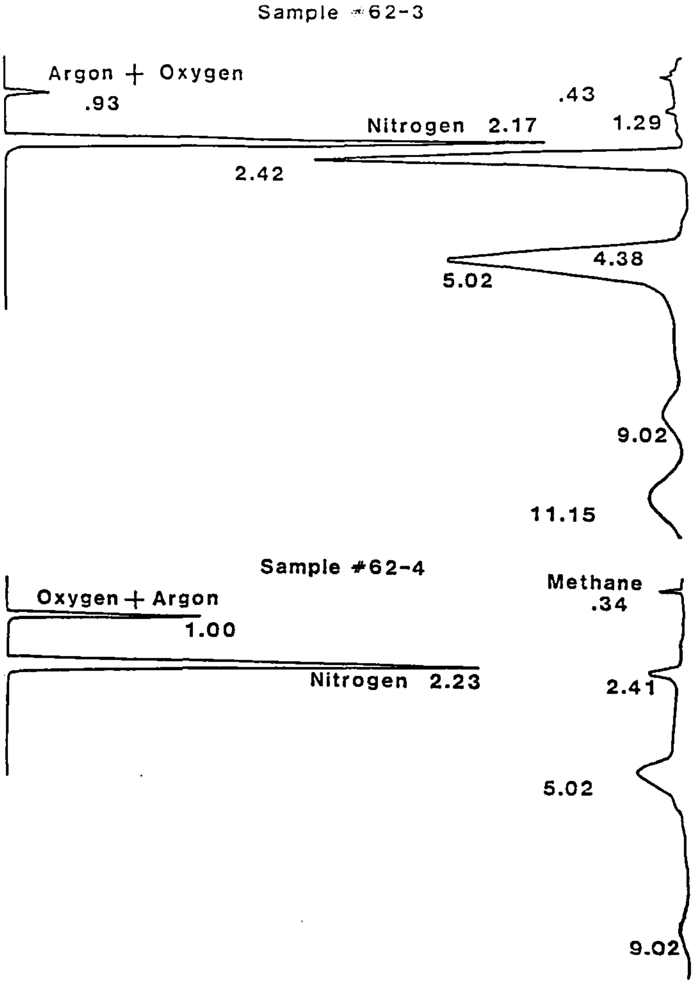

Figure 2 Example chromatograms for two water samples.

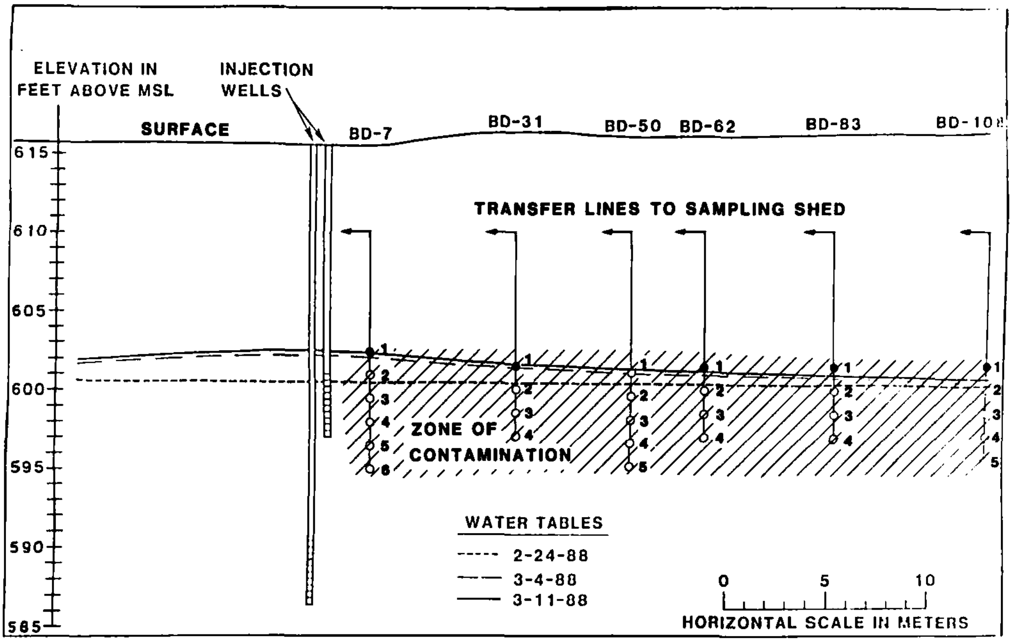

Figure 3 Cross section of pilot scale wells in plume containing gasoline at a remediation site.

first 13 were samples generated in the lab. The rest were collected from an aquifer contaminated with aviation gasoline which was being remediated by injection with water equilibrated with nutrients and pure oxygen. A cross section of the wells are shown in Figure 3. Levels ranged from <0.5 to $32\,\mathrm{mg\,O_2/liter}$. Methane levels were low where detectable. Aromatic hydrocarbons (BTXs) were determined on the aliquot of headspace-displaced water using a Hewlett-Packard Headspace Sampler and 5890 GC/FID. The Winkler titrations were performed within minutes of collection. The samples labeled "w/HCl" were preserved by adding 0.15 ml of 1:1 water:12 M hydrochloric acid solution. Aquifer samples were taken on 3/11/88 and 5/26/88. Analysis by GC was done on 3/14/88 and 5/31/88.

Acid preservation both extended holding time and maintained integrity of samples. Large oxygen depletions occurred in a 30 day storage test for two of three samples not preserved with HCl (Table 3). A comparison by linear regression through the origin of the two dissolved oxygen methods is shown in Figure 4. A distinct correlation existed between the two methods as indicated by coefficient $R^2=0.998$ for 20 sets of real number data after exclusion of less than values.

CONCLUSION

The headspace equilibrium technique was successfully used for routine analyses of dissolved oxygen, methane, and indirectly BTXs. Liquid or solid matrix consti-

Table 2 Dissolved oxygen, methane, and aromatic hydrocarbons in water samples

Sample	*Winkler-O_2 mg/l*	*GC-O_2 mg/l*	*Methane mg/l*	*Total*[a] *BTXs mg/l*
1	2.1	2.54, 2.58	—	—
2	2.4	3.58	—	—
3	8.8	9.36, 9.32	—	—
11	<0.5	0.25	—	—
12 replicate of 11	<0.5	0.42	—	—
21	6.9	7.53	—	—
22 replicate of 21	6.9	7.44	—	—
31	7.6	8.00	—	—
32 replicate of 31	7.7	8.16	—	—
33 replicate of 31	7.7	7.87	—	—
41	8.2	8.52	—	—
42 replicate of 41	8.1	8.64	—	—
43 replicate of 41	8.0	8.15	—	—
48A-5	13.6	15.0	0.005	<0.006
48A-5 replicate	14.6	15.1	0.004	<0.006
31-2	<0.5	0.25	0.002	0.073
31-3 w/HCl	<0.5	0.61	0.004	0.045
31-4 w/HCl	31.9	33.1	<0.002	<0.006
48A-3	1.8	1.94	0.002	0.017
62-3	<0.5	0.49	<0.002	0.072
62-4	4.2	3.68	0.004	0.006
50B-2	<0.5	0.34	<0.002	0.0031
50C-2 w/HCl	<0.5	0.71	<0.002	0.038
7A-2-1	5.9	6.35	0.004	<0.006
7B-4-3	2.2	2.64	0.004	<0.006
7A-2-2	10.7	11.3	0.005	<0.006
7A-2-3	10.8	10.0	0.005	<0.006

[a] Includes summation of results for benzene, toluene, ethylbenzene, *m,p*, and *o*-xylenes, and 1,2,4-trimethylbenzene.

Table 3 Dissolved oxygen change in field samples after 30 days storage at 4 °C by GC-HET

Initial Winkler mg O_2/l	*No HCl mg O_2/l*	*With HCl mg O_2/l*
3.9	<0.1, 0.48	4.52, 4.50
12.2	0.63	11.6, 11.5
5.8	4.95, 5.15	5.74, 6.07

tuents should not interfere with the integrity of the headspace phase. Although the argon chromatogram peak was not separated from the oxygen peak, the additive introduction can be compensated for by reducing D.O. values by a constant. The technique will enable analysis of one bottle of water sample for three chemically different parameters. Because of its convenience and reliability, our headspace equilibrium technique with HCl preservation will be used for routine analysis of dissolved oxygen on samples from both field and lab studies.

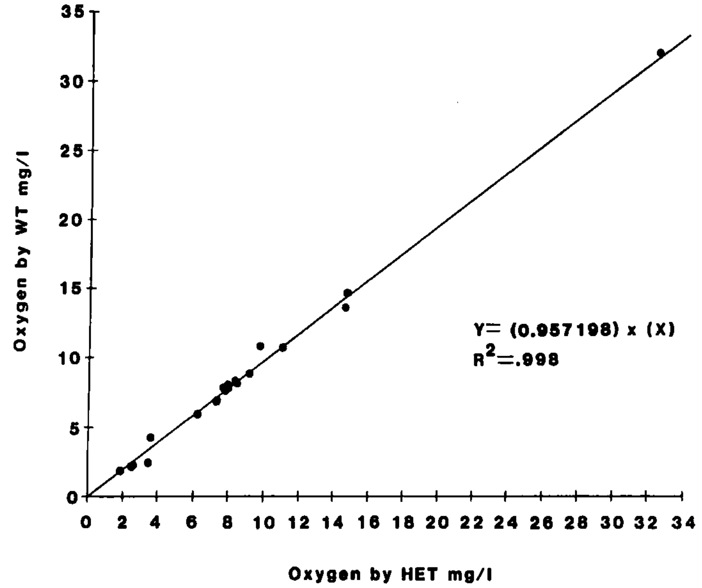

Figure 4 Comparison of dissolved oxygen measurements by Winkler titrations (WT) and headspace equilibrium technique (HET).

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