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STANDARD OPERATING PROCEDURE

Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique

1. Disclaimer:

This standard operating procedure has been prepared for the use of the Ground Water and Ecosystems Restoration Division of the U.S. Environmental Protection Agency and may not be specifically applicable to the activities of other organizations. **THIS IS NOT AN OFFICIAL EPA APPROVED METHOD.** This document has not been through the Agency's peer review process or ORD clearance process.

2. Purpose (Scope and Application):

This method is applicable to the preparation of water samples for determination of dissolved gases. After quantitation of gas equilibrated into the prepared headspace, this method permits calculation of the concentration of the dissolved gas in the water before equilibration. Resulting concentrations are expressed as mg/L and μ g/L of dissolved gas in water. This method has been used for determining dissolved hydrogen, methane, ethylene, ethane, propane, butane, acetylene and nitrous oxide. The number of analyses that can be performed in an eight hour day depends upon the method used to determine the target analyte, 40-60 samples may be analyzed for methane, ethylene, and ethane in eight hours.

This method is restricted to use by or under the supervision of analysts experienced in sample preparation, the use of gas chromatography and the interpretation of chromatograms. Knowledge of Microsoft Excel spreadsheet data entry and macro programming is also a prerequisite to processing quantitation files.

3. Method Summary:

A water sample is collected in the field or in the laboratory in a serum bottle and capped using a Teflon faced septum and a crimp cap of the appropriate size to fit the bottle. If headspace has not already been created by the originator then headspace is created in the lab by the analyst displacing 10% of the water with high purity helium. If the headspace is created by the originator then the headspace volume needs to be provided to the analyst. The bottle is shaken for five minutes and a headspace sample is injected onto a gas chromatographic column where the gaseous components are separated and detected by a thermal conductivity detector, a flame ionization detector or an electron capture detector. The concentration of dissolved gas in the

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original water sample is determined by using the Henry's law constant, the concentrations of the gas in the headspace, the bottle volume, and temperature of the sample. Excel macros and Excel worksheets are provided to aid in the calculations.

4. Reagents:

N/A

5. Equipment/Apparatus:

serum bottles
butyl rubber Teflon faced septum
20-gauge needle
10-mL glass syringe
8-cm 20-gauge needle
10-mL ground glass syringe
thermometer
rotary shaker
steel tubing
two-stage regulator

6. Health and Safety Precautions:

There are no additional precautions that need to be taken other than those in keeping with standard laboratory practices.

7. Interferences:

N/A

8. Procedure:

Sample analysis is described in RSKSOP-194 for methane, ethane, ethylene, propane, butane, and acetylene, RSKSOP-212 for hydrogen and RSKSOP-231 for nitrous oxide.

Water samples should be collected in the field or prepared in the lab by placing the water in a glass bottle. Typically, a 60-mL serum bottle is used. Add the water down the side of the bottle so as not to agitate the sample. Fill to the top and cap using a butyl rubber Teflon faced septum and the appropriate size aluminum crimp cap. Care should be taken so there are no headspace or

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bubbles in the bottle. Field samples should be fixed with 1:1 hydrochloric acid to a pH less than 2 or trisodium phosphate (0.1 grams per 10 milliliters) to a pH greater than 10 before they are capped. The samples should be stored at 4°C and analyzed within 14 days of collection.

Remove samples from refrigerator and allow them to come to room temperature. To generate headspace in the sample bottle, insert through the septum a 20-gauge needle attached to a 10-mL glass syringe set at zero mL. Then an 8-cm 20-gauge needle attached to a section of stainless steel tubing with a needle valve is inserted through the septum. The stainless steel tubing is attached to a two-stage regulator on a cylinder of high purity helium and the helium flow is adjusted using the needle valve to 5 mL per minute or less.

The helium forces water out of the bottle and into the glass syringe. The amount of water taken out of the bottle should be 10% of the volume of the sample bottle. The bottle volume is usually printed on the bottle mottle serum bottle. Another way to determine the bottle volume is to weight the bottle empty, fill it with water, and weigh it again. The difference between the two weights in grams is the bottle volume in milliliters. After the appropriate amount of water has been removed, pull the 8-cm needle out of the septum. Next, pull the syringe from the septum. The sample bottle is then shaken at 1100 rpm on a rotary shaker for five minutes to allow the gases to equilibrate between the headspace and the liquid phase. Measure and record the room temperature. A portion of the headspace is then taken immediately for analysis on the gas chromatograph. Use a 10-mL ground glass syringe with a stopcock to take a 2-mL sample of the headspace. This is done by inserting the syringe needle into the septum so that the side port of the needle is in the headspace. Pull the plunger up to the 2-mL mark a couple of times and then pull it up to the 2-mL mark and close the stopcock and withdraw the needle from the septum and inject the sample into the GC.

9. QA/QC:

Prior to starting analysis, at least one calibration standard for each gas should be analyzed to check calibration. The analyzed values should be within 15% of the expected value. Also, helium should be analyzed to determine if there are any background levels of the analytes. The helium run should contain no analytes of interest at or above the method detection limit. If this condition is met, then analysis may proceed. MDL(method detection limit) data can be found in RSKSOP-194(3).

The data quality objective for the continuing calibration check standards is 85-115%.

For dissolved gas analysis, a method blank comprised of RO water is prepared in exactly the same way as samples and should be analyzed before starting analysis of any samples containing water. This blank is used to determine if background analyte concentrations or interferences are present in

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the analytical system.

QC operations, frequency, control limits and description of corrective actions.

Operation Check	Frequency	Control Limits	Corrective Action
Helium Blank	Before any series of standards	at or below MDL	Repeat blank analysis until objective is met or obtain adequate blank gas.
Method Blanks	Before any series of standards	at or below MDL	Repeat blank analysis until objective met or obtain adequate quality blank water.
Macro Check Test	should be done with every report	none	Reload master macro into Excel spreadsheet.
Continuing Calibration Check	First, last and every 15 samples	85-115% of true value	Check calibration by analyzing additional standards. Recalibrate if standards fail. Reanalyze affected samples; flag data to indicate reanalysis was performed.
Duplicate Sample	after every 15 samples	≤ 20 RPD	Reanalyze samples. Flag data if objective remains unmet.
Second Source QC Standard	At end of sample set	8 5 - 1 1 5 % recovery	Check calibration by analyzing additional standards. Recalibrate if standards fail. Reanalyze affected samples; flag data to indicate reanalysis was performed.

Field or trip blanks, when provided, are prepared in exactly the same way as samples. The presence of target analytes in the field or trip blanks should be noted in the analytical report as long as the

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helium and water blanks met their DQOs, no corrective action for field or trip blanks is required.

Laboratory duplicate injections of the headspace from the same sample should be analyzed every ten samples. The acceptance criteria for lab duplicates is that the two values should be less than 20 relative percent difference (RPD).

Field duplicate samples are collected from the same site at the same time and analyzed under identical conditions.

Quality control gas standards from sources different from calibration standard suppliers should be analyzed within the sample queue. Alternatively, standards from the same supplier as the calibration standard supplier may be used, but the QC standards must have different lot numbers from the calibration gases. The DQO is that measured concentrations be between 85-115% of the expected value.

To test the macros to see if they are working correctly, input 25 in the temperature column, 60 in the bottle volume column, 6 in the headspace column and 10.000 in the column under methane. After the calculation is complete the number under the methane in mg/L, in water column should read 0.0010. This test should be done for every report.

10. Calculations:

10a. General Equations:

According to Henry's law, 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. This implies that when a headspace is created above a water sample, gases which are in the water will equilibrate between the headspace and the aqueous phase. In this method the total gas concentration (TC) in the original water sample is calculated by first determining the gas concentration of the headspace, converting this to the partial pressure of the gas and then using this partial pressure to calculate the aqueous gas concentration which partitioned into the gas phase (C_{AH}), and aqueous phase concentration which remained in the aqueous phase (C_{A}). The total concentration (TC) in the aqueous phase is then:

$$TC = C_A + C_{AH}$$

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where TC = total concentration of gas in the original aqueous sample C_{AH} = aqueous gas concentration in headspace after equilibrium C_{A} = aqueous gas concentration in water after equilibrium

The concentration in the headspace is determined from calibration curves using standard gas samples. The method for calculating the dissolved gas concentration involves several steps. In this section, the general steps and equations will be given; in section 10c, a specific example for nitrous oxide will be shown. Parameters needed are the concentration of the gas component (C_g) , Henry's law constant (H) for the gas, the temperature of the sample (T, C), the volume of the sample bottle (V_b) , the headspace volume (V_b) , and the molecular weight of the gaseous analyte (MW).

For aqueous gas concentration in water after equilibrium, C_A:

- 1) The concentration of the gas phase component is first determined using a calibration curve which was created by analyzing gas standards. The calibration curve can be constructed using EZChrom software, the Waters Millennium software or from the Hewlett Packard 3396 integrator. The calibration curve provides the concentration of gas expressed in ppm or ppb based on volume of gas in total volume of sample.
- 2) This concentration of gas is converted from ppm to the decimal equivalent of the volumetric concentration, C_g , by multiplying the ppm value by 10^{-6} . (When nitrous oxide is determined, quantitations in the ppb levels are typical. In this case the ppb value is multiplied by 10^{-9} .) A gas concentration of 10 ppm becomes 0.00001 (gas volume/total volume). The partial pressure of the gas at atmospheric pressure, p_g , can be found by multiplying the gas volumetric concentration, C_g , by the atmospheric pressure.

Note: In these calculations, total pressure, p_T is assumed to be equal to 1 atmosphere; therefore, p_g can be expressed with units of atm.

$$p_g = C_g * p_T$$
 Eqn. 1

3) According to Henry's law, at equilibrium the mole fraction of the dissolved gas, x_g , can be determined from the partial pressure of the gas, p_g , and the Henry's law constant, H.

$$x_g = p_g / H$$
 Eqn. 2

For these calculations the Henry's law constant must be expressed in units of atm/mole fraction. Table I provides gas solubility coefficients which can be used to calculate Henry's law constants

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for the gases addressed in this SOP. The coefficients are applicable for sample temperatures between 14 and 40 $^{\circ}$ C.

4) Let $n_g = \text{mole of gas analyte and } n_w = \text{mole of water}$. Then the mole fraction of the dissolved gas can be expressed as

$$x_g = n_g / (n_g + n_w)$$

Rearranging

$$n_g = x_g (n_g + n_w) = (x_g * n_g) + (x_g * n_w).$$
 Eqn. 3

If
$$n_g \ll n_w$$
,

then
$$n_g = x_g * n_w$$
. Eqn. 4

Combining Eqn. 2 and Eqn. 4

$$n_g = n_w (p_g / H)$$

and dividing each side by volume

$$n_g / V = (n_w / V) (p_g / H)$$
 Eqn. 5

5) Since the molar concentration of water, n_w/V , is 55.5 mol/L, then

$$n_g/V = (55.5 \text{ mol/L}) (p_g/H)$$
 Eqn. 6

6) The saturation molar concentration of the gas component, CA is defined as

$$C_A = (n_g/V) (MW)$$
 Eqn. 7

where MW = molecular weight of the analyte, g/mol.

7) Substituting Eqn. 6 into Eqn. 7 and converting to mg/L, the saturation molar concentration becomes gas concentration in the aqueous phase

$$C_A = (55.5 \text{ mol/L}) * p_e/H * MW(g/mol) * 10^3 \text{mg/g}$$
 Eqn. 8

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where the final concentration is expressed in mg/L.

For the aqueous gas concentration in the headspace after equilibrium, CAH:

1) For any gas, its density can be calculated at standard temperature by

$$\rho = [MW / (22.4 \text{ L/mol})] * [273 \text{ K} / (T + 273 \text{ K})]$$
 Eqn. 9
where $\rho = \text{density (g/L)}$ and $T = \text{sample temperature in °C}$

2) For the gas/water sample, the volume of the aqueous phase, V_a is the difference between the bottle volume, V_b and the headspace volume, V_h .

$$V_a = V_b - V_b$$
 Eqn. 10

3) The volume of gas equilibrated into the headspace, A_h , can be determined from the volumetric concentration of the gas, C_g , and the volume of headspace, V_h .

$$A_h = V_h * C_g$$
 Eqn. 11

4) Then the concentration, C_{AH} , of the gas component that was originally in the liquid phase but was then partitioned into the gas phase is

$$C_{AH} = A_h/V_a$$
 Eqn. 12

5) Substituting Eqn. 10 and Eqn. 11 into Eqn. 12

$$C_{AH} = [V_h/(V_b - V_h)] * C_g$$

and multiplying by the gas density expression, Eqn. 9, to convert from concentration units of mL of gas/mL of water to mg of gas/mL of water, the concentration of gas in the water sample partitioned into the headspace, C_{AH}, becomes:

$$C_{AH} = [(V_h/(V_b - V_h))] * C_g * (MW/22.4 L/mol) * [273 K / (T + 273 K)] * 10^3 mg/g$$
 Eqn. 13

Then, combining Eqn. 8 and Eqn. 13

$$TC = C_A + C_{AH}$$

$$TC = (55.5 \text{ mol /L})^* p_g/H^* MW(g/mol)^*10^3 mg/g +$$

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$$[(V_h/(V_b - V_h)] * C_g * (MW(g/mol)/(22.4 L/mol)) * [273 K / (T + 273 K)] * 10^3 mg/g$$

The result will be in units of milligrams of gas per liter of water.

10b. Henry's Law Constant:

Temperature corrected values of the Henry's law constant can be calculated using solubility data provided in Table 1 (Ref. 5) and equation 14. The molar solubility, x_2 , of the gas is calculated using the coefficients, sample temperature in Kelvin and gas constant (R = 1.98719 cal K^{-1} mol $^{-1}$). If it is assumed that the partial pressure is low, ~ 1 atm (i.e., $P_2 = 1$ atm), and that the solubility is less than 10^{-3} then Henry's law can be expressed as equation 15. The assumption of 1 atm then allows calculation of the Henry's law constant by equation 16. The units of H are atm/mol fraction.

$$R \ln X_2 = A + B/T + C \ln T + DT$$
 Eqn. 14
 $X_2 = \exp\{(A + B/T + C \ln T + DT)/R\}$
 $H = P_2/X_2$ Eqn. 15
 $H = 1/[\exp\{(A + B/T + C \ln T + DT)/R\}]$ Eqn. 16

10c. Example Calculation:

Methane will be used as the example in the calculation for dissolved gas concentration in water. From the calibration standards, quantitation of a methane sample gives 2130 ppm (v/v).

Parameters for this example are as follows:

sample temperature =
$$25.0 \,^{\circ}\text{C} = 25.0 + 273\text{K} = 298\text{K}$$

bottle volume = $20.0 \, \text{mL}$
headspace volume = $2.0 \, \text{mL}$

1) From Table 1, the Henry's law constant for methane at 25.0 °C is

$$H_{CH4} = 1/\exp[\{-365.183 + 18106.7/298 + 49.7554 * \ln 298 + -0.00028503 * 298\}/1.98719] = 39841 atm/mol fraction$$

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2) Converting gaseous concentration to partial pressure:

$$C_g = 2130 \text{ ppm} * 10^{-6} = 2.13 \text{ x } 10^{-3} \text{ vol CH}_4/\text{vol sample}$$

so $p_g = C_g * p_T = 2.13 \text{ x } 10^{-3} * 1 \text{ atm} = 2.13 \text{ x } 10^{-3} \text{ atm CH}_4$

3) Using Eqn. 8,

$$C_A = (55.5 \text{ mol/L})^* [(2.13 \text{ x } 10^{-3} \text{ atm } /39,841 \text{ atm}) * 16 \text{ g/mol}] * 10^3 \text{ mg/g}$$

$$C_A = 4.75 \text{ x } 10^{-2} \text{ mg CH}_4/\text{L H}_2\text{O}$$

4) Using Eqn. 13,

$$C_{AH} = [2 \text{ mL} / (20 \text{ mL} - 2 \text{ mL})] * 2.13 \times 10^{-3} * [(16 \text{ g/mol})/(22.4 \text{ L/mol})] * [273 \text{ K} / (25 ^{\circ}\text{C} + 273 \text{ K})] * 10^{3} \text{ mg/g}$$

$$C_{AH} = 15.5 \times 10^{-2} \text{ mg CH}_4/\text{L H}_2\text{O}$$

then $TC = C_A + C_{AH} = 4.75 \times 10^{-2} \text{ mg/L} + 15.5 \times 10^{-2} \text{ mg/L}$
 $TC = 0.203 \text{ mg CH}_4/\text{L H}_2\text{O}$.

11. Miscellaneous Notes:

N/A

12. References:

- 1. Kampbell, D., Wilson, J. and Vandegrift, S. Dissolved Oxygen and Methane in Water by a GC Headspace Equilibration Technique, International Journal of Environmental Analytical Chemistry, Vol. 36, 1991, pp. 249 257.
- 2. Kampbell, D. and Vandegrift, S. Analysis of Dissolved Methane, Ethane, and Ethylene in Ground Water by a Standard Gas Chromatographic Technique, J. Chromatogr. Sci., Vol. 36, 1998, pp. 253 256.
- 3. Gas Analysis by Micro Gas Chromatographs, RSKSOP-194, Revision Number 2.

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- 4. GC/ECD Analysis of Nitrous Oxide in Gaseous Samples, RSKSOP-231, Revision Number 1.
- 5. Wilhelm, E., Battino, R. and Wilcock, R. Low Pressure Solubility of Gases in Liquid Water, Chemical Reviews, Vol. 77, April 1977. pp. 219 261.

Appendix: Dissolved Gas Concentration Calculations and Report Processing

Calculation of the results is done using macros written in Microsoft Excel spreadsheets. An example of a data sheet is provided in Figures 1 and 1A. To start the process, the file which contains the master spreadsheet and macros is opened and saved using a file name describing the technical directive and sample set identification. Sample names, gas concentrations from the quantitation program, sample temperature, sample and headspace volumes and sample or check standard identifiers are entered into the spreadsheet. Before processing the samples, the name of the gas, the molecular weight and solubility coefficients are copied into cells J2:O2 The data in the top part of the spreadsheet are linked to the lower portion of the sheet where a nested logic statement filters the data to determine whether it is a sample or check standard, evaluates the magnitude of the sample to determine if it is below the lowest calibration standard and finally calls a macro to perform the calculations described in section 10 above. Cell G30 shows an example of this statement.

Table 1.		Gaseous Molecular Weights, Coefficients for gaseous Solubility Calculation in the Equation								
	$R \ln X_2 = A$	$R \ln X_2 = A + B/T + C \ln (T/K) + DT*$ and Examples of Calculated Henry's Law Constants.								
Gas	Mol. Wt.	А	8	С	D	Henry's Law Constant atm/mol fraction (25 ⁰ C)				
Hydrogen	2	-357.802	13897.5	52.2871	-0.02989360	70,719				
Methane 🗸	16	-365.183	18106.7	49.7554	-0.00028503	39,769				
Acetylene	26	-311.014	16215.8	42.5305		1,333				
Ethylene 🗸	28	-303.888	15817.6	40.7591		11,616				
Ethane 🖍	30	-533.392	26565.0	74.6240	-0.00457313	29,771				
Oxygen	32	-286.942	15450.6	36.5593	0.01876620	43,414				
Propane 🗸	44	-628.866	31638.4	88.0808	18000000000000000000000000000000000000	36,809				
Nitrous Oxide	44	-180.950	13205.8	20.0399	0.02385440	2,272				
Butane	58	-639.209	32785.7	89.1483		45,275				
Carbon Dioxide	44.0	-317.658	17371.200	43.0607	-0.00219107	Management (1971) 1800/001 (1970) 1970/000 (1970) 1970/000 (1970) 1970/000 (1970) 1970/000 (1970) 1970/000 (1970)				
	*Wilhelm e	t al. (1977), C	hem. Rev. 77;	219-262	R=1.98719 cal l	<-1 mol-1; T in Kelvins				

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The macro "DISGAS" provided in Figure 2 uses parameters located in cells in the spreadsheet to calculate the concentration of the dissolved gas. Before the macro returns the result to the spreadsheet, the magnitude of the result is evaluated to determine the correct number of significant figures with which the result should be expressed.

Two columns of concentration values are provided. The first column, column F, gives the concentration of the gas in the water in the sample and column H gives the concentration of the gas in the headspace. These concentrations are expressed in mg/L or ug/L and ppm or ppb (vol/vol). The logic statement shown in cell F71 determines if the concentration is for a gas standard or dissolved gas sample. If it is a check standard, the macro "SIGFIG" is used to express the calibration result with the correct number of significant figures.

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Figure 1. Microsoft Excel Spreadsheet Used to Input Quantitation and Processing Information and to Calculate Dissolved Gas Concentrations.

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Figure 1A. (QC Data Page) Microsoft Excel Spreadsheet Used to Input Quantitation and Processing Information and to Calculate Dissolved Gas Concentrations.

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