

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 µg/L of dissolved gas in water. This method has been used for determining dissolved hydrogen, methane, ethylene, ethane, propane, butane, acetylene, nitrogen, nitrous oxide and oxygen. 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 without headspace, in a serum bottle and capped using a Teflon faced septum and a crimp cap of the appropriate size to fit the bottle. A headspace is prepared in the lab by displacing 10% of the water with high purity helium. 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 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 bubbles in the bottle. Field samples should be fixed with 1:1 hydrochloric acid to a pH less than 2 or 1% trisodium phosphate 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 bottom of the 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. 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.

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

For dissolved gas analysis, a laboratory reagent 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 the analytical system.

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

Operation Check	Frequency	Control Limits	Corrective Action
Method Blank	Before any series of standards	at or below MDL	Repeat blank analysis until objective met or obtain adequate quality blank water or gas.
Continuing Calibration Check	First, last and every 15 samples	85-115% of true value	Check calibration equipment function. Reanalyze affected samples
Duplicate Sample	after every 10 samples	≤ 20 RPD	Reanalyze samples. Flag data if objective remains unmet.
Second Source QC Standard	At end of sample set	85 - 115 % recovery	Check calibration equipment function. Reanalyze QC standards. If DQO remains unmet, determine cause. Recalibrate, reanalyze affected samples if possible.

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 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).

$$RPD = \frac{[(\text{Sample Concentration (ppmv)} - \text{Duplicate Concentration (ppmv)})]}{[(\text{Sample Concentration (ppmv)} + \text{Duplicate Concentration (ppmv)})]/2} * 100$$

Field duplicate samples are collected from the same site at the same time and analyzed under identical conditions. RPDs will be reported for field duplicates, but no corrective actions will result from the RPD values.

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.

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:

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

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_h), 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.

$$p_g = C_g * p_T \quad \text{Eqn. 1}$$

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.

$$x_g = p_g / H \quad \text{Eqn. 2}$$

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 for the gases addressed in this SOP. The coefficients are applicable for sample temperatures between 14 and 40 °C.

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

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

Rearranging

$$n_g = x_g (n_g + n_w) = (x_g * n_g) + (x_g * n_w). \quad \text{Eqn. 3}$$

If $n_g \ll n_w$,

$$\text{then } n_g = x_g * n_w \quad \text{Eqn. 4}$$

Combining Eqn. 2 and Eqn. 4

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

and dividing each side by volume

$$n_g / V = (n_w / V) (p_g / H) \quad \text{Eqn. 5}$$

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

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

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

$$C_A = (n_g/V) (MW) \quad \text{Eqn. 7}$$

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

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

where the final concentration is expressed in mg/L.

For the aqueous gas concentration in the headspace after equilibrium, C_{AH} :

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

$$\rho = [MW / (22.4 \text{ L/mol})] * [273 \text{ K} / (T + 273 \text{ K})] \quad \text{Eqn. 9}$$

where ρ = density (g/L) and T = 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 .

$$V_a = V_b - V_h \quad \text{Eqn. 10}$$

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 .

$$A_h = V_h * C_g \quad \text{Eqn. 11}$$

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

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

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:

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

Then, combining Eqn. 8 and Eqn. 13

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

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

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

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 ($R = 1.98719 \text{ cal K}^{-1} \text{ mol}^{-1}$). If it is assumed that the partial pressure is low, $\sim 1 \text{ atm}$ (i.e., $P_2 = 1 \text{ atm}$), 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.

$$R \ln x_2 = A + B/T + C \ln (T/K) + DT \quad \text{Eqn. 14}$$

$$x_2 = \exp\{(A + B/T + C \ln (T/K) + DT)/R\}$$

$$H = P_2/x_2 \quad \text{Eqn. 15}$$

$$H = 1/[\exp\{(A + B/T + C \ln (T/K) + DT)/R\}] \quad \text{Eqn. 16}$$

10c. Example Calculation:

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

Parameters for this example are as follows:

sample temperature = 25.0 °C
bottle volume = 20.0 mL
headspace volume = 15.0 mL

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

$$H_{N_2O} = 1/\exp\{[-180.950 + 13205.8/(25.0 + 273) + 20.0399 * \ln(25.0 + 273) + 0.02385440 * (25.0 + 273)]/1.98719\} = 2,270 \text{ atm/mol fraction}$$

2) Converting gaseous concentration to partial pressure:

$$C_g = 2130 \text{ ppb} * 10^{-9} = 2.13 * 10^{-6} \text{ vol N}_2\text{O/vol sample}$$

$$\text{so } p_g = C_g * p_T = 2.13 * 10^{-6} * 1 \text{ atm} = 2.13 * 10^{-6} \text{ atm N}_2\text{O}$$

3) Using Eqn. 8,

$$C_A = (55.5 \text{ mol/L}) * [(2.13 * 10^{-6} \text{ atm} / 2,270 \text{ atm}) * 44 \text{ g/mol}] * 10^3 \text{ mg/g}$$

$$C_A = 2.29 * 10^{-3} \text{ mg N}_2\text{O/L H}_2\text{O} = 2.29 \text{ } \mu\text{g N}_2\text{O/L H}_2\text{O}$$

4) Using Eqn. 13,

$$C_{AH} = [15 \text{ mL} / (20 \text{ mL} - 15 \text{ mL})] * 2.13 \times 10^{-6} * [(44 \text{ g/mol}) / (22.4 \text{ L/mol})] * [273 \text{ K} / (25 \text{ }^\circ\text{C} + 273 \text{ K})] * 10^3 \text{ mg/g}$$

$$C_{AH} = 1.15 \times 10^{-2} \text{ mg N}_2\text{O/L H}_2\text{O} = 11.5 \text{ } \mu\text{g N}_2\text{O/L H}_2\text{O}$$

$$\text{then TC} = C_A + C_{AH} = 2.29 \text{ } \mu\text{g/L} + 11.5 \text{ } \mu\text{g/L}$$

$$\text{TC} = 13.8 \text{ } \mu\text{g N}_2\text{O/L H}_2\text{O}.$$

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.
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. 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. 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.

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 G 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

Table 1. Gaseous Molecular Weights, Coefficients for gaseous Solubility Calculation in the Equation: $R \ln x_2 = A + B/t + C \ln(T/K) + DT^*$ and Examples of Calculated Henry's Law Constants.						
Gas	Mol. Wt.	A	B	C	D	Henry's Law Constant atm/mol fraction (25°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
Nitrogen	28	-327.850	16757.6	42.8000	0.01676450	95,411
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		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
* Wilhelm et al. (1977), Chem. Rev. 77; 219-262 R=1.98719 cal K ⁻¹ mol ⁻¹ ; T in Kelvins						

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.

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

	A	B	C	E	F	G	H	I	J	K	L	M	N	O
1	Sample		CH4	PPG	TC	Bottle vol.mL	Headspace mL	Gas		Mol wt.	A	B	C	D
2	EUG 1		721.980	0.000721980	25	75	7.5	Methane		16	-365.183	16106.7	49.7564	-0.00286503
3	EUG 2		1084.815	0.001084815	25	75	7.5							
4	EUG 3		1523.921	0.001523921	25	75	7.5							
5	EUG 4		863.832	0.000863832	25	75	7.5							
6	EUG 5		1183.774	0.001183774	25	75	7.5							
7	EUG 6		1208.078	0.001208078	25	75	7.5	Gas		Mol Wt.	A	B	C	D
8	EUG 6		8496.144	0.008496144	25	75	7.5	Hydrogen		2	-357.802	13397.5	52.2871	-0.029693360
9	EUG 7		1791.691	0.001791691	25	75	7.5	Methane		16	-365.183	16106.7	49.7564	-0.000286503
10	EUG 8		3030.481	0.003030481	25	75	7.5	Acetylene		26	-311.014	16715.8	42.5305	0.000000000
11	EUG 9		3077.294	0.003077294	25	75	7.5	Nitrogen		28	-327.850	16715.8	42.5000	0.01676450
12	EUG 10		1363.895	0.001363895	25	75	7.5	Ethane		30	-533.392	26965.0	74.8240	-0.00467313
13	EUG 10		1378.614	0.001378614	25	75	7.5	Oxygen		32	-286.942	15450.8	36.5593	0.01678620
14	EUG 12		1410.988	0.001410988	25	75	7.5	Propane		44	-628.866	31638.4	88.0808	0.000000000
15	SHAW ENVIRONMENTAL, Inc. Analytical Services Results Report													
16	Laboratory:	QC	Report Date:	4-May-2004										
17	Technical Director:	OLA-6380						Sample Results (1)						
18	Analyst:	Lee Hudson												
19	Method:	RSKSOP-184 & RSKSOP-178												
20														
21														
22	Lab Sample ID	Date Collected	Date Analyzed	Field Sample ID	Data	DF	DF							
23	2402-1	25-Feb-2004	20-Apr-2004	EUG 1	0.068	1	722	1						
24	2402-2	25-Feb-2004	20-Apr-2004	EUG 2	0.104	1	1090	1						
25	2402-3	25-Feb-2004	20-Apr-2004	EUG 3	0.146	1		1						
26	2402-4	25-Feb-2004	20-Apr-2004	EUG 4	0.062	1	654	1						
27	2402-5	25-Feb-2004	20-Apr-2004	EUG 5	0.113	1	1180	1						
28	2402-5 Lab Dup	25-Feb-2004	20-Apr-2004	EUG 5	0.115 (RPD=1.75)	1	1210 (RPD=2.5)	1						
29	2402-6	25-Feb-2004	20-Apr-2004	EUG 6	0.805	1	8470	1						
30	2402-7	25-Feb-2004	20-Apr-2004	EUG 7	0.170	1	1790	1						
31	2402-8	25-Feb-2004	20-Apr-2004	EUG 8	0.288	1	3030	1						
32	2402-9	25-Feb-2004	20-Apr-2004	EUG 9	0.378	1	3980	1						
33	2402-10	25-Feb-2004	20-Apr-2004	EUG 10	0.130	1	1380	1						
34	2402-10 Lab Dup	25-Feb-2004	20-Apr-2004	EUG 10	0.131 (RPD=1.6)	1	1380 (RPD=1.6)	1						
35	2402-10 Field Dup	25-Feb-2004	20-Apr-2004	EUG 12	0.134	1	1410	1						
36	The data quality objective (DQO) for the preparation of laboratory duplicate samples is a relative percent difference (RPD) of 5% for methane as specified in the SOP. The lab duplicates readily met the precision DQO. RPDs for field duplicates were not calculated.													
37														
38														
39														
40														
41														
42														
43	Notes: 1. If the parameter was detected above the quantitation limit (QL), the numeric result is reported; BDL denotes that the parameter was not detected at or above the quantitation limit; BDL () denotes that the parameter was detected above the method detection limit (MDL) but below QL, and the estimated numeric result is reported in parentheses; ND denotes that the parameter was not detected at all. All the results are connected with dilution factors (DF), if applicable. Below method detection limit (MDL). 2. " " " denotes that the information is not available or the analyte is not analyzed.													
44														

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

	A	B	C	E	F	G	H	I	J	K	L	M	N	O
46	Sample													
47	100 ppm CH4	cs	Methane	PFG					TC	Bottles vol./mL	Headspace/mL			
48	Helium Blank	cs	0.000											
49	100 ppm CH4	cs	96.692											
50	1000 ppm CH4	cs	1067.952											
51	10000 ppm CH4	cs	10328.286											
52	100 ppm CH4	cs	101.555											
53	1000 ppm CH4	cs	1072.819											
54	100 ppm CH4	cs	93.612											
55	H2O Blank	s	0.000	0	0.000	0			25	75	75			
56														
57	SHAW ENVIRONMENTAL, Inc.													
58	Analytical Service Results Report													
59	Laboratory:	GC	Report Date:	4-May-2004										
60														
61	Technical Directive:	QA-Q-4980												
62														
63	Analyt:	Lisa Hudson	Analytes											
64			Codes											
65	Method:	RSKSOP-175 & RSKSOP-176	Unit	ppm, v/v in gas										
66			MDL	0.42										
67			QL	10										
68	Data Analyzed	Additional ID	Date Prepared	QC Sample ID	Data	True Value	% REC	% REC	True Value	% REC				
69	20-Apr-2004	CCC	21-May-2002	100 ppm CH4	98.0	100	98.0	98.0						
70	20-Apr-2004	MB	20-Apr-2004	Helium Blank	ND									
71	20-Apr-2004	CCC	21-May-2002	100 ppm CH4										
72	20-Apr-2004	CCC	11-Sep-2001	1000 ppm CH4	1070	1000	107	107						
73	20-Apr-2004	CCC	11-Sep-2001	10000 ppm CH4	10300	10000	103	103						
74	20-Apr-2004	CCC	21-May-2002	100 ppm CH4	102	100	102	102						
75	20-Apr-2004	CCC	11-Sep-2001	1000 ppm CH4	1070	1000	107	107						
76	20-Apr-2004	CCC	21-May-2002	100 ppm CH4	93.6	100	93.6	93.6						
77	20-Apr-2004	MB	20-Apr-2004	H2O Blank										
78														
79	Comments:	The data quality objective (DQO) for the helium Method Blank (MB) is that there should be no response for methane. The DQO for the water MB is that any detected target gases should be <10 ppm. The DQO for the accuracy of CCCs and second source OC standards is 95-115% recovery. These DQOs were met for all the OC samples in this sample set. Matrix spike samples were not present and the requirement to analyze matrix spikes is being removed from the SOP (RSKSOP-175) due to the fact that a spiked gaseous analyte would partition between the liquid and gas phase and not yield good recoveries.												
80														
81														
82	Notes:													
83		1. MB - Method Blank. CCC - Continuing Calibration Check. A calibration standard analyzed within the batch of samples. LCS - Laboratory Control Spike. A laboratory blank spiked with analytes at known concentrations. MS - Matrix Spike. A field sample spiked with known concentrations of analytes. The field sample ID is provided. OC standards obtained from the second source are identified by their designated names. DUP - field sample duplicate analysis. A sample selected by the lab analyst to be analyzed as a duplicate. It is reported in the sample result section. % REC-Percent Recovery. Calculated as the percentage of the results to the true values. It equals to accuracy for CCCs and second source OC standards.												

```
DISGAS
=ARGUMENT("PG")
=ARGUMENT("MW")
=ARGUMENT("VB")
=ARGUMENT("T")
=ARGUMENT("VH")
=ARGUMENT("AA")
=ARGUMENT("BB")
=ARGUMENT("CC")
=ARGUMENT("DD")
=1/(EXP((AA+BB*(T+273)+CC*LN(T+273)+DD*(T+273))/1.98719))
=((55.9*(PG/A11)*(MW*1000))-((VH*(VB-VH))*PG*MW/(22.4*(273*(T+273))*1000))
=IF(A12<0.1,FXED(A12,4),IF(A12<1,FXED(A12,3),IF(A12<10,FXED(A12,2),IF(A12<100,FXED(A12,1),IF(A12<1000,FXED(A12,0),IF(A12<10000,FXED(A12,-1),FXED(A12,-2)))))))
=RETURN(A13)
```

Figure 2. Excel Macro "DISGAS" Used to Calculate Dissolved Gas Concentrations and Determine Significant Figures of the Result.

```
=SIGFIG
=ARGUMENT("S")
=IFS<0.01,FXED(S,4),IFS<0.1,FXED(S,3),IFS<1,FXED(S,2),IFS<10,FXED(S,2),IFS<100,FXED(S,1),IFS<1000,FXED(S,0),IFS<10000,FXED(S,-1),FXED(S,-2))
=RETURN(A3)
```

Figure 3. Excel Macro "SIGFIG" Used to Determine Significant Figures of a Result.