

Measurement of Gas in Groundwater

ALFRED H. HARDER

U. S. Geological Survey, Lake Charles, Louisiana

W. R. HOLDEN

Louisiana State University, Baton Rouge

Abstract. Two methods are used to detect the presence of methane gas in water from wells in southwestern Louisiana. A commercially developed combustible gas indicator proved reliable when using proper collection and analytical techniques and mathematical formulas, provided no hydrocarbons other than methane are present. Data obtained from a gas-entrapment device showed that methane is the only hydrocarbon occurring in these waters. Values obtained for the quantity of methane present utilizing both methods agree within 10%. To aid the better understanding of the use of these two methods and to demonstrate what physical constants are used, the equations utilized in calculating the amount of methane are derived.

INTRODUCTION

Methane gas reportedly occurs in fresh groundwater in California, Illinois, Wisconsin, and Louisiana. Methane in groundwater is probably more widespread than is known; the presence of this gas is not always recognized because little information on detection techniques has been published. As methane gas can constitute an explosion hazard, the determination of the occurrence and amount of methane gas in groundwater is an important part of the groundwater study in southwestern Louisiana. The purpose of this paper is to describe methods and formulas used to determine the amount of gas in fresh groundwater in southwestern Louisiana. Specifically, this paper describes the theory and presents a formula enabling data obtained from a combustible gas indicator to be used. In addition, a gas-entrapment device is described and an equation for calculating the amount of a specific gas in fresh water using spectrometer analyses is given. The reliability of each method is summarized.

The data used in this report were collected as a part of the cooperative groundwater program with the Louisiana Department of Public Works and the Louisiana Department of Conservation, Geological Survey.

COMBUSTIBLE GAS INDICATOR

Theory. Rossum *et al.* [1950] used data obtained from a combustible gas indicator to determine the concentration of methane gas in water in California. Equation 1, which they used to calculate the amount of methane in water, was reanalyzed to determine what physical constants were used in its derivation.

$$W = P[0.257(V_g/T) + 890(V_l/H)] \quad (1)$$

where

- W = weight of methane, mg.
- P = partial pressure of methane, mm Hg.
- V_g = volume of gas phase, cc.
- T = system temperature (absolute), °K.
- V_l = volume of liquid phase, cc.
- H = Henry's law constant, mm Hg per mole fraction.

The use of equation 1 assumes that equilibrium conditions exist between the methane gas in the liquid phase and the partial pressure of methane gas in the vapor phase above the liquid phase. The following analysis relates the concentration of methane in a water sample to the partial pressure of methane in the gas above the water.

Assume that three-fourths of a gallon of fresh water, which contains some methane gas in solu-

tion, is added to a closed container of 1-gallon capacity that originally is filled with dry air. If the container is sealed and allowed to stand for some time, some of the dissolved methane will evaporate into the air space above the water until an equilibrium condition is reached. At equilibrium the partial pressure of methane in the vapor phase is related to the molar concentration of dissolved methane in the liquid phase. For infinitely dilute solutions and at very low pressures (near atmospheric in this case), Henry's law is applicable and

$$P = HX \quad (2)$$

where P = partial pressure of methane in vapor phase, mm Hg; X = mole fraction of methane in the liquid phase; and H = Henry's law constant, mm Hg per mole fraction.

For a particular gas-liquid system at low pressure, the constant H is a function of temperature only. Representative values of H (in mm Hg per mole fraction) and their equivalent reciprocals s (in ppm/atm) are given in Table 1 for the methane-water and nitrogen-water systems.

If the partial pressure of methane in the vapor phase is known, the total weight of methane in the system can be calculated in the following manner. For the vapor phase, at low pressure, the ideal gas law is sufficiently accurate:

$$PV_g = nRT = (W_v/M)RT \quad (3)$$

where

- n = (W_v/M) = moles methane.
- P = partial pressure of methane, mm Hg.
- V_g = volume of vapor phase, cc.
- W_v = weight of methane, g.
- M = 16.043, molecular weight of methane, g/mole.
- T = system temperature (absolute), °K.
- R = 62,360 (cc, mm Hg) per (mole, °K), a universal constant.

Upon rearranging equation 3, the weight of methane in the vapor phase is

$$W_v = \frac{PMV_g}{RT} = \frac{P(16.043)V_g}{62,360T}$$

$$= P\left(0.000257 \frac{V_g}{T}\right) \text{ grams}$$

or

$$W_v = P[0.257(V_g/T)] \text{ mg} \quad (4)$$

By Henry's law, the mole fraction of dissolved methane (X) in the liquid phase is

$$X = P/H \quad (5)$$

As the concentration of dissolved methane in water is extremely small, the molecular weight

TABLE 1. Henry's Law Constants for Methane and Nitrogen
(Calculated using data from Perry [1941], p. 1127)

Temperature, °C	Methane		Nitrogen	
	H , mm Hg/mole fraction	s , ppm/atm	H , mm Hg/mole fraction	s , ppm/atm
0	17.0×10^6	39.8	40.2×10^6	29.5
5	19.7	34.4	45.4	26.2
10	22.6	30.0	50.8	23.4
15	25.6	26.4	56.1	21.2
20	28.6	23.7	61.1	19.4
25	31.4	21.6	65.7	18.1
30	34.1	19.8	70.2	16.9
35	36.9	18.3	74.9	15.9
40	39.5	17.1	79.0	15.0
45	41.9	16.2	82.8	14.3
50	43.9	15.4	85.9	13.8
60	47.6	14.2	91.2	13.0
70	50.6	13.4	95.0	12.5
80	51.8	13.1	95.8	12.4
90	52.6	12.9	95.8	12.4
100	53.3	12.7	95.8	12.4

and density of the liquid phase may be considered the same as that for pure water: a molecular weight of 18.015 g/mole and a density of 1 g/cc. The total moles of water (n_s) in the liquid phase can hence be obtained from the expression

$$n_s = V_s(1)/18.015 \quad (6)$$

where n_s = total moles in liquid phase, and V_s = volume of liquid, cc.

The number of moles of methane in the solution is so low that as a first approximation the number of moles of water in the solution may be taken as the total number of moles of all species in the solution. With these considerations, equations 5 and 6 may be multiplied to obtain an expression for the moles of dissolved methane in the liquid phase, n ,

$$n = Xn_s = \frac{P}{H} \times \frac{V_s \times (1)}{18.015} \quad (7)$$

Multiplication of this last equation by the molecular weight of methane will yield the weight of methane in the liquid phase.

$$W_s = 16.043n = P \frac{(16.043V_s)}{18.015H} \text{ grams}$$

or

$$W_s = P \frac{(890V_s)}{H} \text{ mg} \quad (8)$$

Finally, for the total weight of methane in the system (both vapor and liquid phases), equations 4 and 8 are added to obtain equation 1, repeated here as a convenience:

$$W = P[0.257V_g/T + 890(V_s/H)] \text{ mg}$$

The total weight of methane in the system, as calculated from equation 1, was contained originally in a water sample of volume V_s . Therefore, the concentration of gas in the original sample was W/V_s mg/cc, or $1,000W/V_s$ mg/liter, equivalent to parts per million. Methane concentration, C , in ppm in the water sample is then

$$C = 1,000P[0.257(V_g/TV_s) + (890/H)] \quad (9)$$

Equation 9 requires a knowledge of the partial pressure of methane in the vapor phase P . If V_f represents the volume fraction of methane in the vapor and \bar{P} the total pressure of the vapor (the system pressure or 760 mm Hg at sea level), then

$$P = V_f\bar{P} \quad (10)$$

and equation 9 can be written as

$$C = 1,000(V_f\bar{P}) [0.257(V_g/TV_s) + (890/H)] \quad (11)$$

Equipment and procedure. The Model 40 combustible gas indicator measures the per cent of combustible gases in air with the LEL (lower explosive limit) of pentane gas as a reference. To determine the per cent methane in a gas, a corrected meter reading must be used. Calibration curves giving corrected meter readings for methane are provided by the manufacturer of the instrument. In southwestern Louisiana the absence of combustible gases other than methane favors the use of the combustible gas indicator. As the LEL for methane in air is taken as 5.3% methane by volume [*Mine Safety Appliance Company*, no date], a corrected reading of 100% indicates that the vapor contains 5.3% methane by volume. The corrected meter reading of the instrument is then multiplied by 0.053 to obtain V_f , which is the volume fraction of methane present in the vapor phase. Thus

$$V_f = S/100 \times 0.053 \quad (12)$$

where S = corrected meter reading of instrument (a per cent). Substitution of equation 12 into equation 11 gives for methane gas

$$C = (0.53S\bar{P})(0.257V_g/TV_f + 890/H) \quad (13)$$

Water samples from wells are collected in 1-gallon glass milk bottles, calibrated in increments of 1, 2, and 3 quarts. (See Figure 1.) Laboratory equipment used to determine the quantity of methane in a sample is illustrated in Figure 2. The following laboratory procedure is suggested:

1. Allow the sample to adjust to room temperature.
2. Enter in the appropriate columns on data sheet (Figure 3) the date collected, well number, temperature of water at time of collection, line pressure in discharge pipe at sampling point, aquifer sampled, and volume ratio of gas to water in sample bottle.
3. Shake the sample vigorously for 1 minute and record time.
4. Allow the sample to stand 2 hours. This interval allows an equilibrium to be established between the gas in solution and the gas in the air space above the water.
5. Turn on the vacuum pump and adjust to about 3 inches of vacuum.

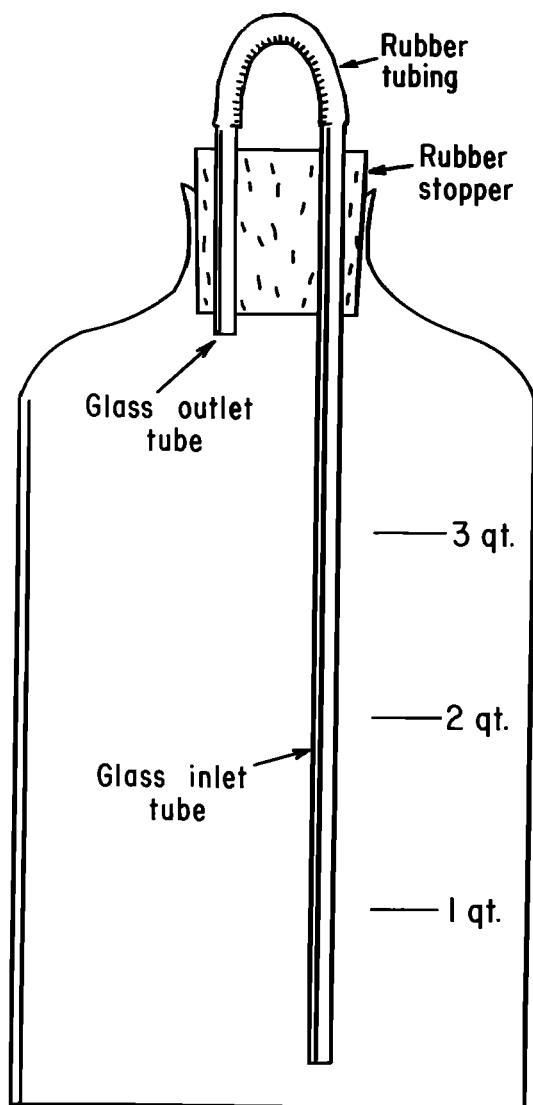


Fig. 1. Sample bottle.

6. Turn on the combustible gas indicator and adjust the meter to zero with air passing through the instrument.

7. Purge the rubber tube on sample bottle of entrapped water by squeezing.

8. Quickly connect the indicator to the short glass outlet tube in sample bottle, read the maximum steady deflection of the meter, and record as per cent LEL.

9. Remove the stopper from the sample bottle, measure and record the water temperature.

10. Determine S , from the manufacturer's

chart for instrument, using the value obtained in step 8.

Calculations. The methane concentration in water from well Cu-627 was computed by use of equation 13 and data from Figure 3:

$$\begin{aligned}
 C &= (0.53S\bar{P}) \quad 0.257 \frac{V_g}{TV_s} + \frac{890}{H} \\
 &= (0.53 \times 77 \times 760) \quad \left(0.257 \times \frac{1}{296} + \frac{890}{30.4 \times 10^6} \right) \\
 &= 28 \text{ ppm methane in the water sample}
 \end{aligned}$$

when $S = 77\%$ (corrected combustible gas indicator meter reading), $\bar{P} = 760$ mm, $V_g = 2.00$ liters, $V_s = 2.00$ liters, $T = 296^\circ\text{K} = 23.3^\circ\text{C} = 74^\circ\text{F}$, $H = 30.4 \times 10^6$.

GAS-ENTRAPMENT DEVICE

Equipment and procedure. The gas-entrapment device makes possible the collection and measurement of all gases released from ground-water pumped to land surface. The instrument (Figure 4) consists of a constant flow-regulating valve, three 4-liter glass bottles, a gas buret, and a $\frac{1}{4}$ -liter leveling bottle filled with a confining liquid (a suitable confining fluid can be obtained by mixing 95 grams of water, 5 grams of concentrated sulfuric acid, and 20 grams of sodium sulfate), all interconnected with stopcocks and tubing. In practice, the instrument, with the exception of the gas buret and its attached reservoir of confining fluid, is completely filled with water from the well. The flow-regulating valve is adjusted to a constant flow of water through the system; a flow of about 1–3 liters per minute provides the best results. This flow is maintained until sufficient gas accumulates for measurement; the time required depends on the quantity of gas dissolved in the water. In southwestern Louisiana, the required time ranged from 15 minutes to 24 hours. A gas sample for composition analysis is obtained by connecting a gas-sampling tube to the gas vent tube of the gas buret.

The gas collected in gas-sampling tubes can be analyzed by one of several methods. Because of the relatively low cost, accuracy, and reproducibility of results, gas samples collected in southwestern Louisiana were analyzed by a commercial laboratory utilizing a mass spectrometer.

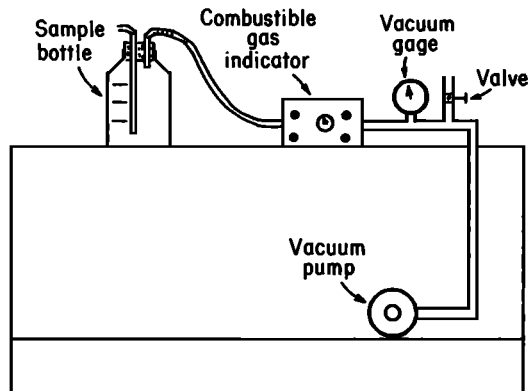


Fig. 2. Sketch of equipment used to determine methane concentrations.

**COMBUSTIBLE GAS INDICATOR LABORATORY FORM FOR
GAS DETERMINATION**

Date of determination: October 7, 1963

By: A. B. Jones

FIELD DATA						LABORATORY DATA						
Date collected	Well numbers		Well water temp. (°F)	Line press. (psig)	Formation screened	$\frac{V_g}{V_s}$	Shake time	Read time	% LEL	S	Lab. water temp. (°F)	Methane (ppm)
	USGS No.	Company No.										
6/4/63	Cu-627	GSU 3	74	100	"500-foot" sand	$\frac{2}{2}$	2:49 p.m.	4:52 p.m.	84	77	74	28

Fig. 3. Data sheet for methane analysis.

Results of analyses are reported in mole per cent of each constituent. (See Table 2.)

The procedure using the entrapment device is:

1. Connect constant-flow valve to closed well discharge line using rubber tubing. To vent air from system close valve D, open valves A, B, and C, and turn on water.

2. After air has been vented from system close valves A, B, and C, and open valve D. Note the time; this is the time when gas will start accumulating in the three bottles. Adjust flow through the system to 3 liters per minute; the

rate of flow should be checked periodically to ensure constancy. Record water temperature after it has stabilized.

3. To start transferring the accumulated gas into the buret for measuring, open valves A and B. This transfers gas from bottles 1 and 2 into bottle 3.

4. After all the gas is in bottle 3, close valves A and B, and record the time.

5. To evacuate air from gas buret, adjust valve C and raise the bottle containing displacing fluid.

6. To evacuate all water from the line between

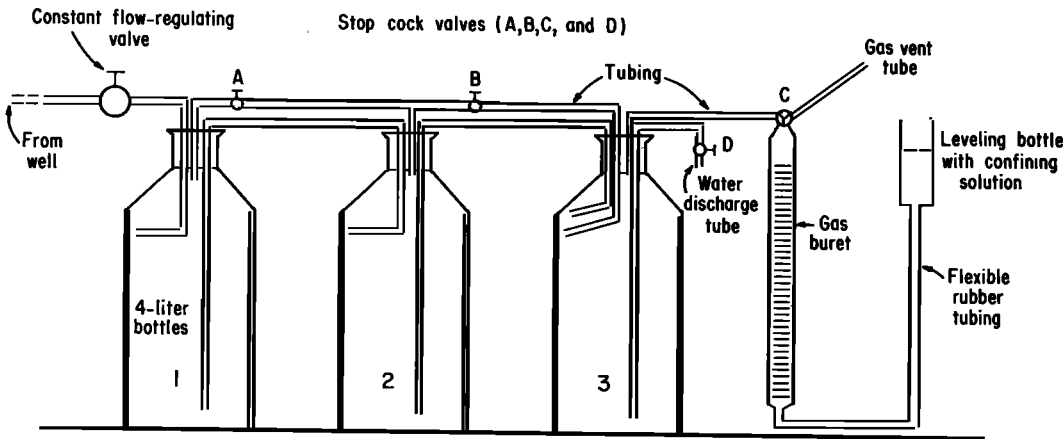


Fig. 4. Sketch of gas-entrapment device.

TABLE 2. Analysis of Gas from Well Cu-627

Gas Analysis			
Well number:	Cu-627	Parish:	Calcasieu, Louisiana
Date:	June 3, 1963	Collected by:	S. M. Rogers
Diameter of screen:	8 inches; casing:	12 inches.	
Screened interval (in feet):	488-558		
Remarks (method of sampling, temperature of water, etc.):			
Gasometer, 76°F.			
Method of analysis:	Mass Spectrometer (in per cent)	Date of analysis:	6/6/63
Methane	73.04	Oxygen	0.02
Ethane	0.00	Carbon dioxide	0.93
Propane	0.00	Nitrogen	25.60
Butane	0.00	Hydrogen sulfide	0.00
Hexane	0.00	Inert gases (by differences)	0.00
Hydrogen	0.00	Argon	0.41

bottle 3 and valve C, readjust valve C. Do not allow any gas to escape while doing this.

7. Use valve C to move gas from bottle 3 into and almost filling the gas buret.

8. Hold the leveling bottle against the gas buret so that the liquid level in both containers is the same. This ensures that the gas volume is measured at atmospheric pressure.

9. Record volume of gas in the buret.

10. Raise the leveling bottle and turn valve C to vent this first charge of gas from the buret.

11. To measure all the gas in bottle 3 repeat steps 7 through 10. The sum of gas measurements made in the buret is the total gas evolved from the water passing through the device during the time lapse between steps 2 and 4. Although some

small amount of gas accumulates in bottle 3 while the gas is being measured, the amount accumulated is, in our experience, so small that it can be neglected.

12. A sample of the gas can be obtained by connecting a gas sampling tube to the gas vent tube on the buret. When doing this, always fill the sampling tube with the confining solution, then displace this confining fluid with gas to ensure collection of an uncontaminated gas sample.

Calculations. The concentration of methane, or any other gas, present in a water sample can be calculated using data from the entrapment device, the gas composition analysis, and equation 14, which was adapted from the work of Hodges *et al.* [1963, p. 14].

$$C = \frac{273VyD_m}{TQtD_w} + sy \quad (14)$$

where

- C = methane concentration, ppm.
 V = gas volume collected by entrapment device, cc.
 y = mole fraction methane in gas phase.
 D_m = density of methane at STP (standard conditions of pressure and temperature, 760 mm Hg and 0°C), g/liter.
 T = system temperature (absolute), °K.
 Q = rate of water flow through system, liters/min.
 t = time for gas accumulation, min.
 D_w = density of water at temperature T , g/cc.
 s = solubility of methane in water at temperature T , ppm/atm (see Table 1).

Methane concentration in water from well Cu-627 on June 23, 1963, was computed using equation 14 and the following data:

- T = 297.5°K (76°F).
 y = 0.73 mole fraction (taken from mass spectrometer analysis).
 D_m = 0.717 g/liter [Hodgman, 1951, p. 991].
 D_w = 0.997 g/cc [Hodgman, 1951, p. 1790].
 s = 21.8 ppm/atm (see Table 1).
 V = 426.8 cc.
 Q = 1.03 liters/min.
 t = 15 min.
 $C = \frac{273 \times 426.8 \times 0.73 \times 0.717}{297.5 \times 1.03 \times 15 \times 0.997} + 21.8 \times 0.73.$
 $C = 29$ ppm.

RELIABILITY

Although either the combustible gas indicator or the gas-entrapment device may be used to measure the quantity of methane in groundwater, each fills a separate and distinct need. The combustible gas indicator has the following advantages: (1) Many samples from one or more wells can be collected and analyzed in a relatively short period of time. Several hundred samples from throughout southwestern Louisiana have been collected and analyzed utilizing this method. (2) The cost of analysis is small. (3) Small quantities of methane (0.2 ppm) can be detected.

The principal advantages of the gas-entrapment device are: (1) the type and quantities of

each gas evolved from the water can be determined; and (2) the quantity of water being sampled is large, thus providing a more representative sample of the gaseous water.

In both techniques error is most likely to occur either when collecting the sample or when transporting it from the field to the laboratory. When relatively large quantities of gas are present, the water discharged by a well may contain gas bubbles, making collection of a representative sample difficult. This problem can be alleviated by increasing the line pressure, if possible, to keep the gas in solution at the sampling point.

When collecting a sample for analysis by the combustible gas indicator, some of the gas can escape through the opened outlet tube. (See Figure 1.) However, this error, due to loss of gas, can be minimized by obtaining the desired amount of sample quickly.

Samples should be analyzed in the laboratory as soon as possible after collection to alleviate errors caused by the decomposition of gas or by the leakage of gas from the container. Experience indicates that methane may decompose if left in a sample container for more than 3 or 4 days. It may also seep out of the containers. Suitable care should be taken of equipment to ensure that all connections and hoses do not leak.

It should be realized that the combustible gas indicator is sensitive to all combustible gases. The technique utilizing this instrument and presented in this paper is therefore not valid if combustible gases other than methane are in the water.

SUMMARY

Two techniques are used to detect and measure methane gas in water from the fresh-water aquifers of southwestern Louisiana. Readings provided by a combustible gas indicator are used to calculate the concentration of methane in a water sample collected in a 1-gallon bottle. The advantages of this method are: small cost; ease and rapidity with which the concentration of methane in water can be measured; and the ability to detect readily as little as 0.2 ppm methane. A formula is derived and used to compute the amount of methane.

Data from a gas-entrapment device and a mass spectrometer analysis are used to determine the quantity, type, and concentration of gas evolved

from the water. The gas-entrapment device is a gas-water displacement chain consisting of a gas buret, leveling bottle, flow-regulating valve, and three 4-liter bottles. The principal advantages of this method are that the concentration of any or all gases present can be determined and that the large quantity of water sampled provides a more representative determination of the gas in the water.

Major sources of error in either method are loss of gas when attempting to obtain a representative sample of highly gaseous water, and leakage of gas through imperfect connections and hoses.

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