Preparation of Water Sample for Carbon–14 Dating

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ABSTRACT

For most natural water, a large sample is required to provide the 3 grams of carbon needed for a carbon-14 determination. A field procedure for isolating total dissolved-carbonate species is described. Carbon dioxide gas is evolved by adding sulfuric acid to the water sample; the gas is then collected in a sodium hydroxide trap by recycling in a closed system. The trap is then transported to the dating laboratory where the carbon-14 is counted.

INTRODUCTION

An assessment of the carbon-14 concentration of water in various parts of hydrologic systems is useful in determining both direction and rate of water movement. Current interest in carbon-14 measurements has necessitated the development of a field procedure for isolating total dissolved-carbonate species from water systems. This paper describes an adequate yet simple method for readily accomplishing the isolation.

The authors acknowledge the early work by L. L. Thatcher and C. W. Naeser on the water sample preparation technique and thank Irving May for measuring CO_2 content of NaOH traps used in determining the efficiency of the apparatus shown in figure 1.

PRINCIPLES OF ISOLATION

Sulfuric acid added to water samples liberates dissolved-carbonate species as carbon dioxide gas. The evolved gas is collected in a sodium hydroxide trap by recycling in a closed system.

For most natural water, a large sample is necessary to provide the minimum of 3 g of carbon required for an age determination by counting. Polyethylene bags manufactured for use by dairy companies in transporting liquids are suitable for collecting large-volume water samples. These two-ply lightweight containers, designed to hold as much as 6 gallons each, are supported by a cardboard carton provided with the bag. Water is removed without bubbling because the bags collapse as they are emptied; thus air contamination is minimized. Polyethylene carboys bound in plywood have also been used in sample collection and have served as the gas evolution flask during carbonate isolation.

When collecting ground water, adequate care must be taken to reduce air contamination of the sample and to pump the well until a representative sample of formation water is assured.

The apparatus shown in figure 1 was used to obtain sequential evolutions of CO_2 from carefully weighed reagent-grade Na_2CO_3 standards. The overall efficiency of the procedure was determined using a gas-flow rate of approximately 30 cc per sec. In practice, screw compressor clamps on rubber connection lines were used to control the gas-flow rate. Percent of CO_2 recovery as a function of cycle time is plotted on figure 2. To attain a minimum of 90 percent CO_2 recovery, the minimum cycle period should be 150 minutes when using a 5-gallon evolution flask and 180 minutes when using the 13-gallon carboy.

REAGENTS

1. Sulfuric acid, concentrated, reagent grade.
2. Sodium hydroxide, .5N, carbonate free (any method listed):

   a. Dissolve 200 g NaOH (reagent grade, carbonate free) in demineralized CO_2-free water and dilute to 1 liter.

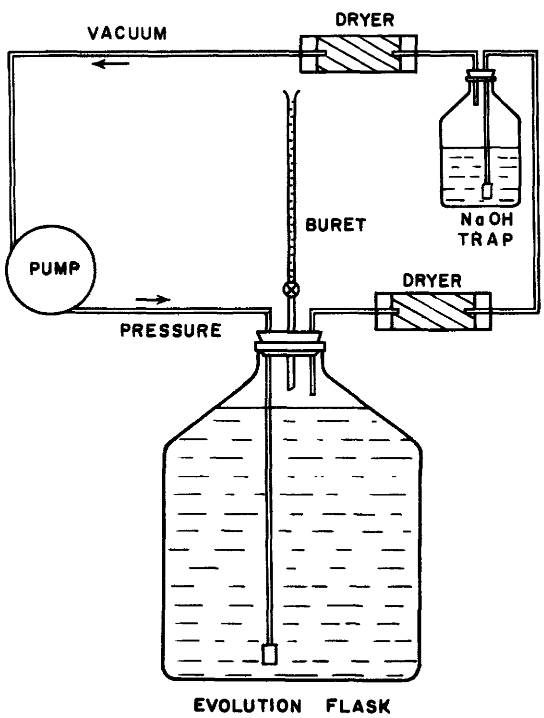

Figure 1.—Apparatus for isolation of dissolved-carbonate species from water.

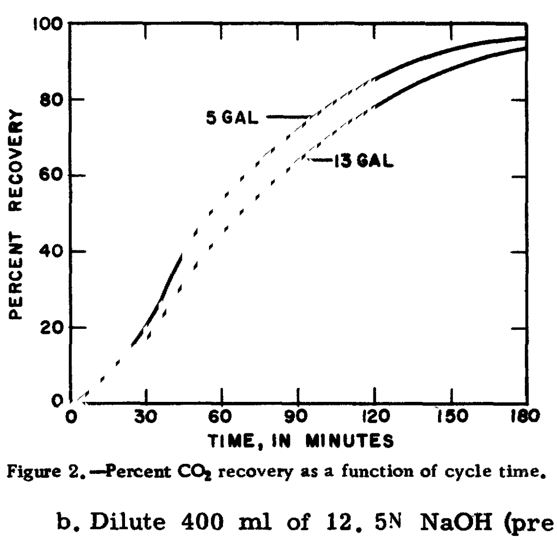

Figure 2.—Percent CO_2 recovery as a function of cycle time.

b. Dilute 400 ml of 12. 5N NaOH (prepared reagent, carbonate-free) to 1 liter with demineralized CO_2-free water; dilute 500 ml of 10N NaOH (prepared reagent, carbonate free to 1 liter, or use 5N NaOH (prepared reagent, carbonate free).

Dissolve 1 g of $SrCl_2 \cdot 6H_2O$ in a minimum of demineralized CO_2-free water and add to the 5N NaOH solution. Stopper container tightly and swirl the mixture. If a precipitate forms, allow it to settle, and use only the clear supernatant liquid. Dispense the sodium hydroxide solution by means of a double-action rubber-bulb pump fitted with a drying tube charged with Ascarite.

3. Silica gel, indicating.
4. Gas, Nitrogen.

APPARATUS

1. a. Bag, water collection, polyethylene, with carton. The Scholle Container Corp. product or its equivalent is recommended.
 or
 b. Bottle, water collection, carboy, polyethylene, $6\frac{1}{2}$ gal or 13 gal capacity.
2. Flask, gas evolution, glass or polyethylene, 5 gal, $6\frac{1}{2}$ gal, or 13 gal capacity.
3. a. Pump, sealed-diaphragm type. The Fisher dynapump 1-092 series is satisfactory.
 or
 b. Pump, peristaltic-action type.
4. Bottle, glass 1 liter.
5. Buret, 10 ml or 25 ml. A separatory funnel may also be used.
6. Tubes, gas dispersion, fritted, medium porosity.
7. Drying tubes, gas.

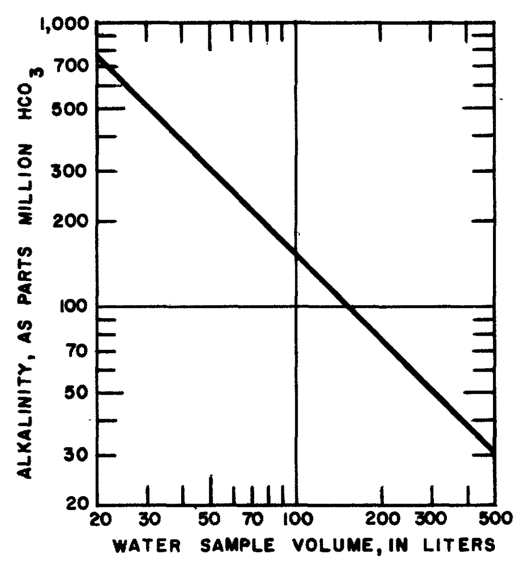

Figure 3.—Relation of alkalinity to minimum water-sample volume required for carbon-14 measurement.

8. Tubing, glass, $\frac{1}{4}$ in. ID.
9. Tubing, rubber, $\frac{3}{16}$ in. ID.
10. Clamp, screw-compressor type.
11. Stoppers, rubber.
12. Plastic sheet. Saran wrap has been used successfully.

PROCEDURE

1. Determine the alkalinity (parts per million as HCO_3^-) of the water to be analyzed. The procedure described by Rainwater and Thatcher (1960, p. 137–140) is appropriate. From figure 3, determine the minimum volume of sample required for carbon-14 measurement.
2. Introduce all or part of the water sample into the evolution bottle which is being swept with nitrogen gas. Connect the bottle to the apparatus shown in figure 1. Minimize the free air space by choosing an evolution vessel that is not excessively large; the free air space should be not more than half a liter. Pack the gas drying tubes with freshly regenerated indicating silica gel.
3. Charge the NaOH trap with at least 300 ml, but not more than 500 ml, of 5N NaOH. The trap should be swept continuously with nitrogen gas while being filled.
4. From figure 4, compute the volume of concentrated H_2SO_4 needed to lower the pH of the water sample to 4.5. The addition of 10 percent excess of acid over the stoichiometric requirement will hasten the evolution and assure nearly complete reaction. Add acid from the buret, close the buret, start the pump, and allow the gas to circulate for the time required (fig. 2) to assure nearly complete evolution and entrapment.
5. Upon completion of the CO_2-evolution cycle, seal the NaOH trap with a plastic covered rubber stopper, wire the stopper in place and transport the trap to the carbon-14 laboratory.

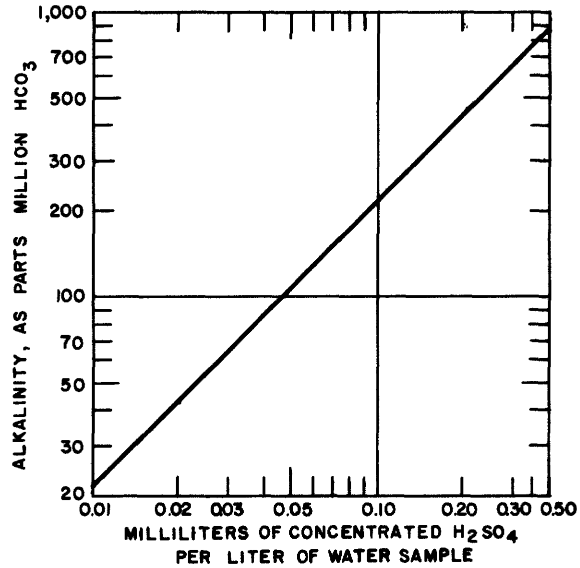

Figure 4.—Minimum volume of concentrated H_2SO_4 required to release CO_2 from water samples of known alkalinity.

REFERENCE

Rainwater, F. H., and Thatcher, L. L., 1960, Methods for collection and analysis of water samples: U.S. Geol. Survey Water-Supply Paper 1454, 301 p.

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