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United States Department of the Interior

U.S. GEOLOGICAL SURVEY

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NATIONAL WATER QUALITY LABORATORY TECHNICAL MEMORANDUM 1996-05

April 5, 1996

To: Assistant Chief Hydrologist for Technical Support
Acting Chief, Office of Hydrologic Research
Regional Hydrologists
Chief, Office of Water Quality
Assistant Chief, Office of Water Quality
Chief, National Water Information System
Acting Chief, NAWQA
Chiefs, Branches of Regional Research
Area Hydrologists
District Chiefs
Regional Water-Quality Specialists
Assistant Regional Hydrologists for NAWQA
District Water-Quality Specialists
Chiefs, NAWQA Study-Units
Chief, Ocala Project Office
Members, Radchem Committee
Chief, Yucca Mountain Project Office
QA Manager, Yucca Mountain Project
Chief, Branch of Technical Development & Quality Systems
Employees, National Water Quality Laboratory

From: Peter F. Rogerson, Chief
National Water Quality Laboratory
Branch of Analytical Services

Subject: Collection, processing, and analysis of carbon isotope samples

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Revision: None

SCOPE

The National Water Quality Laboratory (NWQL) of the U.S. Geological Survey (USGS) has contracted with the University of Waterloo for the analysis of carbon-13 and carbon-14 in solids and in dissolved inorganic carbon (DIC) in water samples.

In addition to the conventional analysis of carbon-14 (by beta counting) and carbon-13 (by mass spectrometric analysis), the new contract includes the analysis of carbon-14 by accelerator mass spectrometry (AMS). The advantages in selecting AMS for carbon-14 determinations over conventional beta-counting procedures are in ease of on-site collection and capability of determining carbon-14 activity in small samples. Conventional beta-counting determinations of carbon-14 usually require at least 5 grams of carbon, with an average reported precision of approximately ± 0.3 percent modern carbon (pmc), while AMS determinations of carbon-14 usually require at least 5 milligrams of carbon, with an average reported precision of about 1 to 3 pmc. On-site collection of samples for beta counting can require 2 to 4 hours--time needed to precipitate sufficient quantities of inorganic carbon from the water--while collection for AMS determinations can be as simple as filling an appropriate container (see below). With the new contract, both the AMS and beta-counting Schedules for carbon-14 will automatically report carbon-13.

For most aqueous samples, Schedule 1000 will probably be more cost effective than Schedule 994. However, if analytical precision is of highest priority, somewhat higher precision may be obtained by beta counting (Beukens, 1992), especially if the sample has a low carbon-14 activity (<5 pmc). Analytical precision, by either beta counting or AMS measurement, depends, in part, on duration of the measurement and sample size. As a general guide, results obtained from AMS determinations of carbon-14 activity of samples submitted to the University of Waterloo and analyzed by AMS under subcontract to IsoTrace Laboratory, Toronto, Ontario, during the past 2 years have had the following 1 sigma analytical precisions: carbon-14 activity >50 pmc, ± 0.7 percent of the reported activity; carbon-14 activity of approximately 20 pmc, ± 0.9 percent of the reported activity; carbon-14 activity of approximately 5 pmc, ± 3 percent of the reported activity. Although AMS technology is capable of much higher precision (Gove, 1992; Beukens, 1992), these services are not provided under the USGS contract. For rocks and other carbonate solids, Schedule 990 will probably be more cost effective than Schedule 960 if the sample contains at least 5 grams of carbon.

All carbon-14 determinations are reported in percent modern carbon (pmc) normalized to the 1950 National Bureau of Standards (NBS) oxalic acid standard (Stuiver and Polach, 1977; Wigley and Muller, 1981), with accompanying 1 sigma error in percent modern carbon. Carbon-13 samples are reported in per mil relative to the Vienna Peedee belemnite (VPDB) standard (Coplen, 1994).

Carbon-14 and carbon-13 analyses are listed in tables 1 and 2.

Table 1

Schedule	Lab Code	Description
1000	2010	Carbon-14 by AMS of DIC (aqueous sample) reported as pmc.
	2011	A one-sigma value (pmc) that reflects the uncertainty due to sample processing and analysis of the carbon-14.
	440	Carbon-13 reported in per mil relative to VPDB.
960	2014	Carbon-14 by AMS of solid carbonate sample reported as pmc.
	2015	A one-sigma value (pmc) that reflects the uncertainty due to sample processing and analysis of the carbon-14.
	2016	Carbon-13 reported in per mil relative to VPDB.

994	1199	Carbon-14 by beta counting of DIC (aqueous sample) reported as pmc
	640	A one-sigma value (pmc) that reflects the uncertainty due to sample processing and analysis of the carbon-14.
	440	Carbon-13 reported in per mil relative to VPDB.
990	2012	Carbon-14 by beta counting of solid carbonate sample reported as pmc.
	2013	A one-sigma (pmc) value that reflects the uncertainty due to sample processing and analysis of the carbon-14.
	2016	Carbon-13 reported in per mil relative to VPDB.

Table 2

Lab Code	Description
440	Carbon-13 on DIC (aqueous sample). Reported in per mil relative to VPDB.
2016	Carbon-13 on a solid. Reported in per mil relative to VPDB.

COLLECTION OF SAMPLES

Schedule 1000

Provide sufficient water sample to contain a minimum of 5 milligrams of dissolved inorganic carbon (DIC). For many water samples, a 250-milliliter sample will be sufficient. The attached figure gives guidelines for sample volumes required to provide a minimum of 5 milligrams DIC for a range of field alkalinities and pH. The two curves on the figure give corresponding alkalinity and pH values for simple inorganic carbonate waters (at 25° C) that would contain 5 or 10 milligrams of DIC in a 250-milliliter volume. If, for example, the sample alkalinity is 150 milligrams/liter (as CaCO₃ or greater, a 250-milliliter bottle fitted with a Teflon/silicon septum is sufficient for most pH. Sample volumes of 1 liter or more will be needed if the field alkalinity is less than 80 milligrams/liter (as CaCO₃ and pH is greater than 7.0. The recommended method of collection is as follows:

Fill the appropriate bottle(s) fitted with Teflon/silicon septum to provide at least 5 milligrams of DIC. Fill the sample container(s) from the bottom of the vessel. Filter the sample to eliminate the possibility of contamination of the DIC with particulates containing carbonate minerals. A 0.45-micrometer standard cellulose nitrate filter is sufficient; silver filters are not needed because DOC normally will not interfere with the carbon-14 determination of DIC. Collect and filter the water sample without contacting air. Establish a closed path from the water source, through the filter, to the bottom of the container. Fill from the bottom, allowing overflow of several liters of

filtered water. For potentially low carbon-14 samples (<10 pmc) or if relatively long times are required for filtering, flush the headspace above the water sample with nitrogen while filling the container. For water samples that are, by all appearance, free of particulates, collect a raw, unfiltered sample. Use glass bottles fitted with a Teflon/silicon septum for most samples. The septum allows laboratory extraction of the water sample without contact with air. Suitable bottles are as follows: 250-milliliter bottles, safety coated (for alkalinity > about 100 milligrams CaCO₃/liter)

Cat. No	Item	Cap Size	#/Case	Cost/Case (\$)
220724	Bottle	24-400	48	101.80
240518	Cap with hole	24-400	200	39.65
240588	Septa for caps with open tops	24 mm	100	113.72

1,000-milliliter bottles, safety-coated (for alkalinity > about 100 milligrams CaCO₃/liter)

Cat. No.	Item	Cap Size	#/Case	Cost/Case (\$)
220726	Bottle	33-430	24	135.01
240540	Cap with hole	33-430	200	58.22
240590	Septa for caps with open tops	33 mm	100	193.88

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A supply of these bottles is maintained in the Ocala Laboratory. Other bottles can be substituted. Virtually any glass bottle would be suitable if fitted with a Teflon/silicon septum, provided on-site personnel can prepare caps with a hole drilled in the center to allow laboratory access to the septum. The Teflon side of the septum should be in contact with the water sample. **LEAVE A SMALL HEADSPACE (1-2 MILLILITER AIR OR NITROGEN) IN THE SAMPLE BOTTLE TO AVOID BREAKAGE CAUSED BY EXPANSION IF THE WATER SAMPLE WARMS.** Secure bottle caps by wrapping with electrical tape. Record the sample alkalinity (in milligrams/liter as CaCO₃) and pH on the sample bottle. Collect the sample in duplicate in case of breakage or other loss prior to analysis. Store the duplicate sample under refrigeration and in darkness to minimize biological activity; otherwise do not preserve it. Carbon-14 samples cannot be stored indefinitely in septum bottles. If samples will be stored for more than 2 months prior to submission, fit the glass bottles with polycone-seal caps (preferably at time of collection) to minimize exchange of CO₂ in the bottle with the atmosphere.

Alternative sampling procedures for Schedule 1000

1. In special cases, such as for very low carbon-14 content (for example, <5 pmc), it might be desirable to collect the AMS water sample in a stainless steel, flow-through vessel. Connect the filtered or raw sample source to the stainless-steel vessel via a closed path (as in above). Suitable vessels include: Whitney Sample Cylinder No. 304L-HDF4-500 (500-milliliter capacity) or No. 304L-HDF4-1000 (1,000-milliliter capacity) with stainless-steel valves (Whitney SS-16DKM4-F4) on each end. Flush several liters through the vessel (from bottom up) before closing (downstream valve first). **THERE IS NO NEED TO LEAVE ANY HEADSPACE IN THE VESSEL.** 2. Historically, USGS personnel have collected carbon-13 samples by direct precipitation on-site using ammoniacal-strontium chloride solution and submitted for analyses by LC440. Continue to collect samples by precipitation on-site, but they must now be submitted under LC440 as washed, dried, and homogenized powders. The contract laboratory will not accept bottles containing precipitates in ammoniacal-strontium chloride solutions. Although reliable results can be obtained using the direct precipitation method, there are several advantages to collection in Teflon/silicon septum bottles over precipitation on-site, including small sample size, ease of collection, eliminates laboratory sample processing of precipitates, and avoids problems in shipping ammoniacal-strontium chloride solutions. However, precipitation using ammoniacal-strontium chloride is well established, as opposed to the gas-stripping method currently being used by the contract laboratory. If on-site personnel have access to a laboratory with a fumehood, it might be advantageous to collect samples as precipitates and process them to clean, dry, homogenized precipitates for analysis by LC440, or Schedule 990 for carbon-14 and carbon-13. The procedure for direct precipitation of strontium carbonate is as follows: Precipitate the sample in a 1-liter glass bottle using an ammoniacal- strontium chloride solution. Arrange to obtain the ammoniacal-strontium chloride solution from the Ocala Laboratory. Alternatively, prepare the ammoniacal-strontium chloride solution by dissolving approximately 500 grams of analytical reagent-grade strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) in 2.5 liters of concentrated analytical reagent-grade ammonium hydroxide solution (approximately 30 percent NH_3) (or in smaller quantities as needed). It is important to let any precipitate that forms settle overnight to the bottom of the bottle because this is most likely strontium carbonate formed from impurities in the reagents or strontium carbonate formed from sorption of CO_2 from the atmosphere. Further purify the ammoniacal-strontium chloride solution by filtration under inert (nitrogen) atmosphere in a fumehood. Use 0.2-10 micrometer pore size glass-fiber filters (Gelman). Store the ammoniacal-strontium chloride solution in glass bottles and keep tightly capped when not in use.

On-site, fill a 1-liter glass bottle (polycone seal) with filtered sample (or raw sample if the water is free of particulates). Flush the bottle from the bottom to overflow with several liters. Then pour off approximately 50 milliliters of water sample and replace with an equal volume of the ammoniacal-strontium chloride solution, being careful to avoid any precipitate that may have formed in the bottom of the ammoniacal-strontium chloride solution. As a further precaution against contamination of the sample, filter the ammoniacal-strontium chloride solution into the sample bottle using a 50-milliliter syringe with flow-through filter and 0.45-micrometer pore size Millipore membrane filter. Caution: **Wear rubber gloves and goggles at all times while preparing or handling the ammoniacal-strontium chloride solution.** A white precipitate of strontium carbonate will form if the sample contains DIC. Hassan (1982) discusses possible interferences, such as water samples containing large concentrations of sulfate. Before submission, the NWQL requires that the strontium carbonate precipitate be filtered and washed with CO_2 -free distilled water under an inert atmosphere. Dry, grind, and homogenize the filtrate by passing it through a 250-micrometer pore size sieve prior to submission under LC440.

Schedule 960

For AMS determination of carbon-14 in solids, a minimum of 5 milligrams C is required; however, if possible, provide sufficient material to contain at least 10 to 20 milligrams C. (For reference, 100 milligrams CaCO_3 contains approximately 12 milligrams C; 100 milligrams SrCO_3 contains approximately 8 milligrams C.) Although solids can be submitted without preparation, it is recommended that the project office provide ground, well-homogenized samples that have been determined to be representative of the material to be analyzed. The contract does not provide for preparation of homogenous, representative samples. To minimize carbon isotopic fractionation, pass each dry strontium carbonate sample through a 250-micrometer pore size sieve. Otherwise, carbon-13 variations of 1 per mil can be observed in aliquots of the strontium carbonate powder from a single sample (Hassan, 1982). A 3-inch stainless-steel sieve works well because it can be washed with dilute HCl, water, and acetone between samples. The strontium carbonate sample will be acidified in an extraction process by the contract laboratory to produce CO_2 for AMS analysis and mass spectrometric determination of carbon-13.

Schedule 994

For beta-counting determination of carbon-14 of DIC in water samples, on-site personnel are responsible for extracting at least 5 grams C from the water. The carbon is normally extracted by precipitation from several hundred liters as strontium carbonate (see Gleason and others, 1969; Hassan, 1982) after pH has been raised to greater than 10.3 using a strong CO_2 -free base (for example, CO_2 -free NaOH). Although there are currently several large precipitators stored in WRD District Offices, it might be necessary to construct a precipitation vessel suitable for collecting the carbon-14 sample. Purchase and preparation of reagents for precipitation is an additional requirement and expense. A nitrogen atmosphere should be in contact with the water sample during precipitation. Two to four hours are normally required for collecting carbon-14 samples by direct precipitation. Alternatively, the extraction could be conducted at the District Office prior to submitting the beta-counting sample to the NWQL. Collect the precipitate in a large bottle attached to the bottom of the precipitator. Seal the bottle containing precipitate and water from the precipitator on-site and ship to the NWQL. Neither the contract laboratory nor the NWQL will extract the DIC directly from water samples collected on-site. The NWQL can provide further details on procedures for processing DIC samples for beta-counting determination of carbon-14.

Schedule 990

For beta-counting determination of carbon-14 in solid samples, sufficient sample is needed to provide at least 5 grams C. Although rock samples can be submitted without preparation, it is suggested that the project office provide ground, well-homogenized samples that have been determined to be representative of the material for analysis (as described in Schedule 960).

Lab Code 440

Lab Code 440 is used only for determination of carbon-13. Water samples may be submitted as outlined in Schedule 1000.

Lab Code 2016

Lab Code 2016 is used only for determination of carbon-13. Solids can be submitted as noted in Schedules 960 or 990.

Use of Schedule 960 for noncarbonate samples

In some cases special arrangements can be made through the NWQL to use Schedule 960 for submission of carbon-bearing solids other than carbonate samples. For example, use Schedule 1000 for AMS determination of carbon-14 activity in DOC samples, provided proper procedures have been followed to collect and prepare the sample prior to submission.

SHIPMENT OF SAMPLES

Samples are to be shipped to the NWQL--not to the contract laboratory. During cold periods, take precautions to ensure that water samples do not freeze during shipment.

TECHNICAL QUESTIONS

Refer technical questions to Niel Plummer (703) 648-5841 and Tyler Coplen (703) 648-5862.

Direct questions pertaining to the contract turnaround times and reporting of results to Ann Mullin (303) 467-8235.

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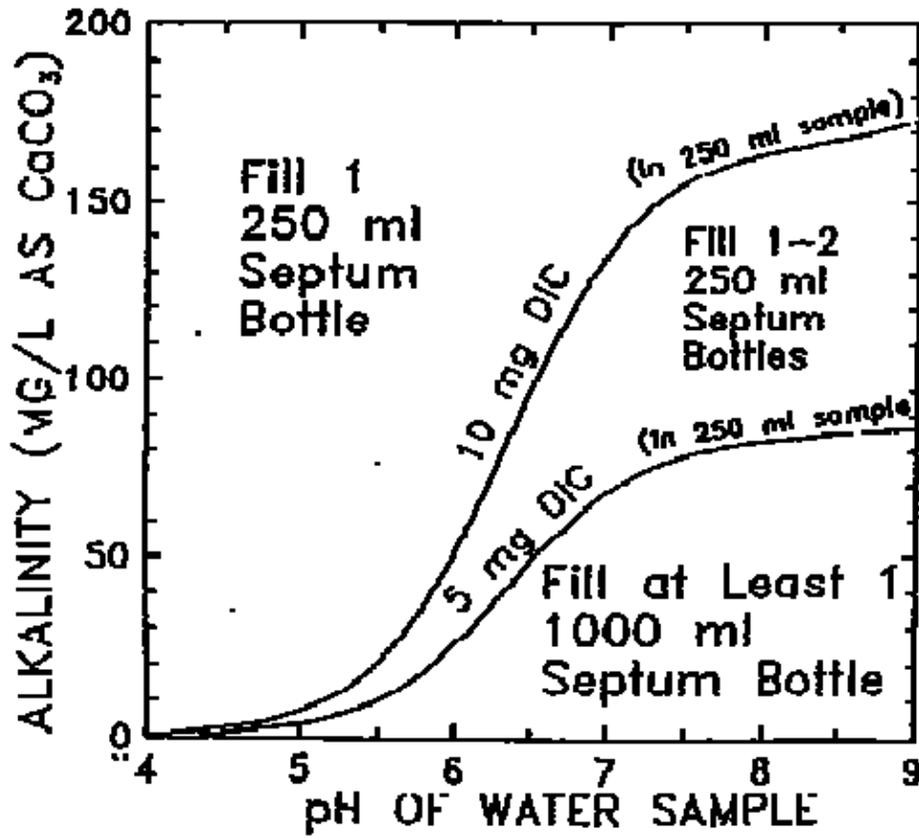
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