Kansas Geological Survey

Analytical Services Section
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COLLECTION, HANDLING AND ANALYSIS OF NATURAL WATERS

Research Program Goals

For any research program in which analytical data are to be generated over the course of the project it is essential that communication between the investigator and the Analytical Services Section begin at an early stage in the formulation of the program. These discussions should focus on topics such as water quality parameters of interest; quality of the data to be generated (general screening to benchmark); analytical procedures to be used; determinations to be made on site, in a field facility, and at the KGS laboratories; and considerations for the collection, preservation, and transport of samples to the point of analysis. Failure to address these issues early on may seriously limit the generation of needed data in a timely, efficient manner and will greatly reduce the section's ability to coordinate analytical work loads within the laboratory.

Collection

The selection of water quality parameters to be determined and the decision of where the determinations will be made dictate the nature of the container and the types of preservation needed, the need for field filtration, and acceptable holding times between collection and analysis of samples for the various constituents of interest. Failure to obtain properly preserved sample aliquots during the collection stage will make it impossible to acquire specified data or to add desired determinations at a later date. As examples, specific conductance and Cl could not be determined if only an HCl-preserved sample was collected for nutrient analyses and trace metals could not be determined later if only a raw unpreserved sample was collected at the time of sampling.

High density plastic bottles are the containers of choice for the collection of water samples used in the determination of most inorganic constituents; however, glass should be used to store samples for the determination of Hg. If the waters contain particulate material (suspended or sediment) field filtration is essential for any aliquots which are to be acid preserved. This prevents undesirable acid-solid interactions which can lead to erroneous data for dissolved species in the waters. If filtration is required, it is important that the filtration equipment be rinsed thoroughly between sampling sites. If multiple aliquots are to be collected at a given

site, it may be desirable to collect a large amount of water in a reservoir and blend it before filling the various aliquot bottles which are required. This will serve to remove "chemical fractionation effects" which might appear as a result of analyses run on aliquots from a given source which are slightly separated in time of collection and general water chemistry.

Raw unacidified and/or acid-preserved aliquots are collected at each sampling site. The bottles containing unpreserved sample aliquots are filled completely in order to minimize loss of dissolved gases and loss of dissolved species between the time of collection and analysis. The acid-preserved aliquots, on the other hand, are filled to a fixed volume which is less than that of the container volume. This facilitates loss of CO_2 and provides for the general control of the acid content of the aliquot to a range suitable for subsequent analyses. Consistency should be maintained in the filling of the bottles if at all possible.

There are several things to avoid during the collection process. Do not collect the first water derived from an idle well system. Pump or bail the well to remove stagnant water, several casing volumes may be necessary to achieve representative formation water. Specific conductance and temperature may serve as guides for beginning the processes of field measurements and sample collection. Do not allow fumes to interact with water being collected as an unpreserved aliquot. Do not collect the waters used for field specific conductance or pH measurements in bottles prepared for the determination of dissolved species, or pour water from an unpreserved aliquot bottle out for field specific conductance or pH measurements and then return it to the bottle. These practices lead to out-gassing and possible contamination of the aliquots involved.

Handling

If samples are transported to a field facility or back to the KGS laboratories for additional analytical work, they should be placed in an ice chest on ice following collection and kept cool until they are delivered to the laboratory facility. Caps should be secured on all bottles before the bottles are placed in the ice chest. The samples should not be allowed to freeze at any time between collection and analysis because of the risk of loss of dissolved constituents from the bottles which have been filled completely.

Samples returned to the KGS laboratories are placed in a refrigerator upon arrival. They are then logged into the laboratory's master record book and assigned laboratory identification numbers. Bottles representing differently preserved aliquots from a single collection at a given site are all assigned the same identification number. Data recorded during the log-in include name of the person submitting the sample, nature of the sample, collection site location, work to be done, date received in the laboratory, and remarks such as date collected, field filtration, presence of particulate material in bottles.

Bottles are removed from the refrigerator and warmed to room temperature prior to being used in a specific analysis, and then are returned to the refrigerator to await further testing. Bottles for all samples are held in the refrigerator until the requested work has been completed and quality control checks such as charge balances have been run. The unacidified aliquots are left in the refrigerator if Br, I, or IO_3 are to be determined; otherwise, at this point all bottles are drained and cleaned for later reuse.

Analysis

Collection of water at a given site for inorganic constituent analyses may yield sample splits as follows: a raw unpreserved aliquot, an HCl-preserved aliquot (2 ml. redistilled 6 M HCl/200 ml. of sample volume), and an HNO_3-preserved aliquot (1ml. redistilled 18 M HNO_3/250 ml. sample volume). Unpreserved aliquots are used for the determination of total dissolved solids (TDS), specific conductance, SiO_2, Ca, Mg, Na, K, Sr, pH, CO_3, HCO_3, SO_4, Cl, F, Br, I, IO_3, and B. HCl-preserved aliquots are used in the analysis of NH_4, NO_3, PO_4, trace metals (except Ag), Se, As, B, SiO_2, and major-minor cation constituents. The HNO_3-preserved aliquots are used for the determination of Ag, trace metals, B, SiO_2, and major-minor cation constituents. The HNO_3-preserved aliquots are also suitable for the analysis of As and Se by graphite furnace Atomic Absorption (AA), but not by hydride-generation AA.

Allowable holding times between collection and analysis and the need to use certain analytical data for concentration estimates in later testing tend to dictate the general order in which individual component analyses are carried out in the course of a complete analytical work-up of a water sample. When it is time to process a batch of samples in the laboratory, all aliquots in the batch which contain particulate material are filtered. If acidified and unacidified aliquots of a given sample contain solids, the unacidified portion is filtered first and then the acidified aliquots, using the same filtration set-up. The filtration equipment is rinsed thoroughly with deionized water between samples having different identification numbers. The acid preserved aliquots are returned to the refrigerator after all filtration is completed.

Specific conductance, pH, CO_3, and HCO_3 are measured on the room temperature unpreserved aliquots. If TDS measurements are required, withdrawl of these samples should be made at this time. Then the bottles are returned to the refrigerator. The HCl-preserved aliquots are now brought to room temperature and PO_4 and NO_3-UV screening measurements are run directly on the acidified waters. The acidified aliquots are refrigerated again. Elevated PO_4 values may result from the acidification of water containing particulate material.

Specific conductance is used to estimate Cl concentrations and prepare appropriate dilutions from the room temperature unpreserved aliquots.

Reduction of the Cl estimates on a molar basis may be necessary when NO_3 levels above 45ppm are encountered and when ground waters exhibit HCO_3 values in excess of 300ppm. Following the determination of Cl, the specific conductance is used in conjunction with the measured Cl values, augmented on a molar basis by NO_3 values above 45ppm and/or HCO_3 values above 300ppm for ground water, to estimate SO_4 levels and prepare appropriate dilutions from the room temperature unpreserved aliquots. The bottles are re-refrigerated after the determination of SO_4.

Estimates of Ca and Na concentration levels are made using the CO_3, HCO_3, Cl, SO_4, and NO_3 data and a first cut of dilution estimates for the major cation analysis by Inductively Coupled Plasma (ICP) is made. SO_4, NO_3 in excess of 45ppm, and HCO_3 up to 300ppm are assumed to be associated with Ca. Chloride and excess HCO_3 above 300ppm are assigned to Na for the estimates. The milliequivalents per liter of the anion species are totaled to obtain milliequivalents per liter, and subsequently ppm, estimates for the respective cation. Next, the specific conductance and SO_4 data are reviewed to insure that the specific conductance and SO_4 levels in samples subjected to ICP analysis will be below 2000 mmho and 100ppm, respectively. Diluted samples are transferred to plastic bottles if SiO_2 and B are to be determined. The aliquots used in the ICP cation analysis are returned to the refrigerator. Out-gassing and increased pH levels may lead to measureable loss of Ca in the unpreserved aliquots if the time interval between the determinations of specific conductance , pH, and HCO_3 and the ICP analysis for cations is more than a few days. The problem is more pronounced for surface waters and ground waters with high HCO_3 levels, >400ppm. Refrigeration helps retard cation loss from the unpreserved aliquots. The acid preserved aliquots are not subject to cation loss in the manner of the unpreserved aliquots. However, they may exhibit elevated cation levels if the waters which were acidified contained particulate material. Changes in water quality during the collection of multi-aliquots at a given sampling site can lead to a poor charge balance in the case where anions are determined primarily from an unpreserved aliquot and the cations from an acid-preserved aliquot. This problem can be minimized by the use of a reservoir to blend a large volume of water which is then used to fill the different bottles required. Correction should be made for the dilution associated with the acidification step if acid-preserved aliquots are used for cation determinations.

Trace metals which are run by AA methods may be determined at any point following log-in of samples and any needed filtration. However, trace metals determined by ICP are generally run after the major components have been completed so that dilutions can be estimated based on the presence of high TDS or SO_4 levels. Elevated trace metal levels may result from the acid preservation of water containing particulate material. Therefore, it is best to filter waters to be acid preserved through a 0.45m filter membrane in the field just prior to the acidification step.

Next, the HCl-preserved aliquots are brought to room temperature and 30ml portions of the waters are brought to about pH 6 by titration with 8N NaOH using a pH meter for end point detection. The HCl-preserved aliquots are returned to the refrigerator following the neutralization of the 30ml sample portions. NH_4 and NO_3 are determined on the pH-adjusted samples. Data from the NO_3-UV screening are used to make dilutions for the NO_3 determinations. Both NH_4 and NO_3 require correction for the dilution associated with the acidification and neutralization steps.

Fluoride is run on room temperature waters from the unpreserved aliquots. The bottles are returned to the refrigerator following the analysis and are retained there pending the verification of data for complete analyses by charge balance checks or later determinations of Br, I, and IO_3. Charge balances make use of data for Ca, Mg, Na, K, Sr, CO_3, HCO_3, SO_4, Cl, F, NO_3, and NH_4; and are generally expected to be within ±2% for waters in which the total milliequivalents per liter of cations plus anions exceeds a value of about 13 milliequivalents per liter. For samples more dilute than this, the imbalance between cations and anions should be no more than about 0.25 milliequivalents per liter.

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