STEP-LEACHING PROCEDURE FOR EXTRACTING SOLUBLE CHLORIDE AND BROMIDE

LOS ALAMOS
QUALITY PROGRAM

APPROVAL FOR RELEASE

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Los Alamos
Yucca Mountain Site Characterization Project

HISTORY OF REVISION

REVISION NO.	EFFECTIVE DATE	PAGES REVISED	REASON FOR CHANGE
R0	06/20/95	N/A	Initial procedure.
R1	09/13/95	6, 8-10, & Att. 1	To simplify the process.
R2	01/09/97	All	Revised to comply with LANL-YMP-QP-06.3 requirements.

STEP-LEACHING PROCEDURE FOR EXTRACTING SOLUBLE CHLORIDE AND BROMIDE

1.0 PURPOSE

This detailed technical procedure (DP) describes a step-leaching procedure for extracting chloride, bromide and other soluble constituents from rock samples in order to determine the intrinsic ratio of these constituents to one another as well as the chlorine isotopic ratio for the Yucca Mountain Site Characterization Project (YMP).

2.0 SCOPE

This DP applies to all YMP personnel who conduct step-leaching of rock samples as part of the YMP's Water Movement Test task for Los Alamos National Laboratory (LANL).

3.0 REFERENCES

LANL-YMP-QP-02.7, Personnel Training
LANL-YMP-QP-03.5, Documenting Scientific Investigations
LANL-YMP-QP-12.3, Control of Measuring and Test Equipment and Standards
LANL-YMP-QP-17.6, Records Management
LANL-CST-DP-95, Preparation of Samples for Chlorine-36 Analysis
LANL-CST-DP-103, Identification, Storage and Handling of Samples for the Water Movement Test
LANL-CST-DP-110, Use of Ion Chromatography to Determine Anion Concentrations

4.0 DEFINITIONS

4.1 Rock Samples

Rock samples are geologic materials intended for laboratory studies or analyses as part of YMP site characterization investigations. Rock samples include, but are not limited to, surface samples, drill cores, drill cuttings, and rocks from underground excavations.

4.2 Leachate

Leachate refers to the aqueous solution obtained by combining deionized water with a crushed rock sample and allowing time for soluble constituents to dissolve in the water.

4.3 Process Blank

The purpose of a process blank is to test for the presence of chloride and chlorine-36 contamination in processing samples for chloride and chlorine

isotopic analyses. A process blank is required to accompany each sample suite. The presence of chloride or chlorine-36 in the process blank may indicate a problem with chloride or chlorine-36 contamination.

5.0 RESPONSIBILITIES

The following personnel are responsible for the activities identified in section 6.0 of this procedure:

- Principal Investigator (PI) for the Water Movement Test
- YMP personnel performing work to the procedure

6.0 PROCEDURE

The use of this procedure must be controlled as follows:

- If this procedure cannot be implemented as written, YMP personnel should notify appropriate supervision. If it is determined that a portion of the work cannot be accomplished as described in this DP, or would result in an undesirable situation, that portion of the work will be stopped and not resumed until this procedure is modified, or replaced by a new document, or until current work practice is documented in accordance with QP-03.5, Section 6.1.6.
- Employees may use copies of this procedure printed from the controlled document electronic file; however, employees are responsible for assuring that the correct revision of this procedure is used.
- When this procedure becomes obsolete or superseded, it must be destroyed or marked “superseded” to ensure that this document is not used to perform work.

6.1 Principle

The ratio of bromide (Br) to chloride (Cl), or of sulfate (SO_4) to Cl, needs to be determined in Yucca Mountain tuffs in order to correct for the effect of rock Cl on diluting the meteoric ^{36}Cl signal during laboratory leaching of rock samples. The Br / Cl or SO_4 / Cl ratio of leachate should closely represent that intrinsic to the rock after repeated leaching, drying, and grinding of the rock to remove the meteoric halides and to release additional rock halides. Details of the leaching procedure described in this DP vary slightly depending upon whether subsequent analyses are only for determination of the Br / Cl or SO_4 / Cl ratio or for analysis of the ^{36}Cl / Cl ratio as well.

6.2 Equipment and Hardware / Software

Material and supplies which may be needed to conduct work by this DP include standard laboratory supplies. Equipment which may be needed to conduct

sample leaching is listed below. Items equivalent to those listed below may be used provided they perform the same function with an acceptable level of performance as judged by the user or the PI. Not all of the following items may be needed for processing any given sample by this DP.

- water purification system capable of producing deionized water with resistivity greater than 17.5 megohm-cm (calibration not required; see section 6.3.2)

- analytical balance with a minimum capacity of 300 g and 1% sensitivity for masses greater than 50 g (calibrated in accordance with QP-12.3)

- shatterbox

- centrifuge

- convection oven capable of maintaining a temperature in the range of 80 to 105 °C (± 5 °C)

- sieve set including mesh sizes of approximately 5 mm, 2 mm, 1 mm, 0.2 mm, and 0.075 mm

- sieve shaker (optional)

6.2.1 Equipment Malfunctions

Any equipment malfunction occurring during implementation of this procedure is likely to be detectable in the course of conducting work and hence is not expected to have a detrimental effect on the final results. The water purification system has a meter that indicates the resistivity of the purified water. This meter is checked prior to use by the user to verify that the resistivity is within the range of acceptable values, i.e., greater than 17.5 megohm-cm. If a problem with any equipment arises which can be considered to be a potential source of error or uncertainty for the results, then it is addressed following section 6.7.

6.2.2 Safety Considerations

Good laboratory and scientific practices are used in the laboratory to protect against injury. Applicable LANL safety practices for conducting laboratory work are followed, as appropriate.

6.2.3 Special Handling

See sections 6.3.3 and 6.3.4.

6.3 Preparatory Verification

6.3.1 Hold Points

See sections 6.5.7 and 6.6.

6.3.2 Calibration

The analytical balance is calibrated and controlled pursuant to QP-12.3. The water purification system does not require calibration because the purpose of its meter is limited to alerting the user to a failure of the system to produce deionized water, as indicated by the reading on the resistivity meter. Meter failure is indicated by a “zero” reading, at which time the meter is replaced by the vendor.

6.3.3 Environmental Conditions

Potential for cross-contamination by sources of chloride and bromide other than those in the sample being processed lies in part with the airborne dust that results from sieving and transferring crushed samples into and out of the shatterbox. To address this concern, a new sample is not opened until the dust from the previous sample has settled, the work space has been wiped with a wet paper towel, and the shatterbox has been cleaned as described in section 6.3.4.2. The user should not touch the sample or the inside of cleaned items with bare hands.

6.3.4 Cleaning and Use of Equipment

To minimize cross-contamination, the sieves, shatterbox, and labware are cleaned prior to processing each new rock sample.

6.3.4.1 Sieves, sieve pan, and sieve lid: Remove particles that can be easily dislodged from the sieve meshes. Wipe the sieve, sieve pan, and sieve lid three times using a paper towel wetted with deionized water. In order to minimize Cl contamination from hands, avoid touching the inner surfaces with bare hands. Each sieve is also inspected to ensure that the mesh is not damaged.

6.3.4.2 Shatterbox: Clean the shatterbox thoroughly by wiping three times with a paper towel wetted with deionized water. All inside parts must be dry before processing a sample. Avoid touching the inside parts with bare hands. Follow manufacturer’s guidelines regarding operation of the shatterbox.

6.3.4.3 New labware: Wash labware initially with a detergent such as Alconox, rinse it with tap water, then rinse it three times with deionized water. Subsequent use requires rinsing three times

with deionized water, unless excessive sample material or non-soluble compounds have contaminated a piece of labware, in which case wash using the procedure for new labware.

6.4 Control of Samples

Sample identification and control must be sufficient to trace a sample and its derivatives from its original field location to the point of analysis, and the integrity of the sample must be safeguarded throughout the entire process. Consequently, the user must be trained to DP-103 before working with samples analytically and must also follow guidelines set forth in that document for sample control.

Step-leaching nomenclature will consist of the sample aliquot ID, assigned per DP-103, followed by -SLn where SL stands for Step Leaching and n is the number of times that this particular aliquot has been leached, starting with 1.

NOTE: Examples of sample identifiers are R220-9-SL2 and R205-3-SL3, where R220-9 and R205-3 are aliquot IDs.

6.5 Implementing Procedure

6.5.1 Sample Withdrawal and Sieving

6.5.1.1 Rock cuttings to be leached by this DP should initially be within the particle size range of 2 to 5 mm, sieved according to 6.5.1.2 and 6.5.1.3. Initial masses are on the order of 100 g for halide analyses and one kg if the $^{36}Cl/Cl$ ratio is to be analyzed as well. These quantities are offered as rough guidelines; more or less material may be processed at the user's discretion. Samples are removed from storage following DP-103.

6.5.1.2 Stack the selected sieve sizes (approximately 2 and 5 mm, corresponding to sieve No. 10 and No. 4) on the top of the pan and cover with the lid. Place the sample in the topmost sieve and secure the lid. Shake the sieves either manually or with a sieve shaker until all particles smaller than the size of interest have passed through that screen.

6.5.1.3 Discard the portion of the sample passing the smallest mesh size. The size retained by the largest mesh size may be either returned to storage or discarded, at the user's discretion. The sample retained by the smallest mesh size is transferred into a sealed container.

6.5.1.4 Process each sample in batches of 500 g or less, combining the fractions retained by the smallest mesh until sufficient material has been obtained.

6.5.2 Leaching Step #1

6.5.2.1 Weigh the sample into one or more preweighed clean Nalgene bottles. One-liter bottles are generally a convenient size with which to work. Record weights with a precision of 1% or better.

6.5.2.2 Add a quantity of deionized water equal in mass to that of the weighed sample. The volume of water added is determined with a precision of 1% or better. Weigh the mixture.

6.5.2.3 Stir or swirl the rock and water mixture at least two or more times over a period of 48 hours.

6.5.2.4 Remove a small fraction of the leachate (20 - 30 ml) for halide analyses following DP-110.

6.5.2.5 Extract as much of the remaining leachate from the mixture as possible by decanting, then record the weight of the leachate. A centrifuge may be used if necessary. Discard the leachate and retain the sample for the next step.

6.5.2.6 Dry the sample in a convection oven at 80 to 105°C until the sample appears completely dry (a minimum of 12 hours). The purpose of the drying is to prevent clumping of the sample in the shatterbox in the following step.

6.5.3 First Sample Grinding

6.5.3.1 Crush the oven-dried sample from the previous leaching step into particle sizes smaller than 1 mm (passing sieve No. 18) using the shatterbox. The sample should be divided into two or three portions during grinding to ensure a uniform grinding. The shatterbox operating time may vary depending on the sample size, but is preferably short (on the order of a few seconds).

6.5.3.2 Sieve the crushed sample through a 1 mm sieve (No. 18) and transfer the sample that passes this sieve back into the original Nalgene bottle.

6.5.3.3 Regrind the coarser fraction retained by the sieve until all the sample passes this sieve, or if the proportion of the sample retained by the sieve is less than 10%, then it may be added to the ground fraction in the Nalgene bottle.

6.5.4 Leaching Step #2

Repeat steps 6.5.2.1 through 6.5.2.6, keeping each sample in its original Nalgene bottle in order to prevent cross-contamination.

6.5.5 Second Sample Grinding

Grind the oven-dried sample from the previous leaching step to a fine powder in the shatterbox by grinding for more than 3 minutes.

6.5.6 Leaching Step #3

Repeat steps 6.5.2.1 through 6.5.2.6, using the same Nalgene bottles. Save the rest of the leachate if ^{36}Cl analysis is desired, for processing following DP-95. The leachates from duplicate samples may be combined for ^{36}Cl analysis. Otherwise, discard the remainder of the leachate.

NOTE: Steps 6.5.2.5 and 6.5.2.6 can be omitted at this point if the user chooses to terminate the process per step 6.5.7.

6.5.7 Termination or Continuation of Process

The user may choose to terminate the procedure at this step: (1) if either Cl or Br concentrations are below detection limits, or (2) if Br/Cl ratios remain constant (e.g., within two standard deviations) for the leachate samples from two consecutive step-leaching steps.

The user may also continue the step-leaching for an additional grinding-leaching sequence by repeating steps 6.5.5 and 6.5.6 if the Br/Cl data indicate that a substantial meteoric component may still be present.

At the end of the step-leaching of a given sample, it is discarded.

6.5.8 Process Blank

6.5.8.1 Because airborne dust is the most likely source of chloride and chlorine-36 contamination, the process blank is prepared using an empty container placed in the convection oven accompanying the processed rock samples during each drying step, following this DP.

6.5.8.2 At the end of sample processing, add about 50 ml of deionized water to the capped bottle and let it sit for 2 days.

6.5.8.3 Set aside 10-20 ml of the rinse water for halide analyses following DP-110. To the remainder of the rinse water, add about 5 mg Cl carrier and process for ^{36}Cl analysis by DP-95, if a ^{36}Cl process blank is required for this batch of samples.

6.6 Data Acquisition and Reduction

Rock and water masses or volumes are determined with a precision of 1% or better, and masses or volumes of recovered leachates with a precision of 10% or

better. Greater uncertainties are acceptable for masses and volumes determined for estimation purposes. Calculations using the data generated following this DP shall be verified by the PI before submission of the results to the Records Processing Center (RPC) per Section 7.0. The acceptability and precision of the data shall also be evaluated by the PI prior to submission of the results to the RPC, taking into account the precision of the instruments used as documented pursuant to QP-12.3.

6.7 Potential Sources of Error and Uncertainty

Careful labeling of containers reduces error due to mislabeling. The possibility of sample contamination is reduced by working in a clean environment. Modifications to this procedure are permitted provided that PI concurrence is obtained prior to implementing the changes. These changes must be documented in accordance with QP-03.5. If a problem arises which can be considered a potential source of error or uncertainty for the results, then it is also documented in the laboratory notebook or logbook in accordance with QP-03.5.

7.0 RECORDS

Proper execution of this DP results in entries in to a scientific notebook or logbook. Attachment 1 lists the information required to be documented. Entries are made in accordance with QP-03.5. The notebook or logbook is submitted as a Quality Assurance record to the RPC in accordance with QP-17.6.

8.0 ACCEPTANCE CRITERIA

The criteria that show that this procedure has been correctly implemented are the entries in section 7.0.

9.0 TRAINING REQUIREMENTS

A prerequisite for this DP is to train to DP-103. This DP requires read-only training. Training of personnel to this DP is documented pursuant to QP-02.7.

10.0 ATTACHMENTS

Attachment 1: Checklist of Laboratory Notebook and Logbook Entries (1 page)

CHECKLIST OF LABORATORY NOTEBOOK AND LOGBOOK ENTRIES

Entries required by DP-103 are made in the appropriate sample inventory logbook at the time of sample withdrawal or return.

Initial descriptive information is entered in the laboratory notebook or logbook as appropriate prior to starting a technical procedure and on a continuing basis as experimental and procedural changes dictate. These entries are:

- reference to this and other relevant DPs, including revision number
- unique identifiers for calibrated equipment used to conduct this DP

In addition to general entries, several parameters need to be recorded in order to evaluate the resulting data. For each leaching step, these entries are:

- sample processed, listed by its unique identifier
- particle size fraction,
- air-dried mass of sample (1% precision or better),
- volume or mass of deionized water added (1% precision or better),
- leaching start and end dates, and
- volume or mass of extracted leachate (10% precision or better).

Finally, the user must record problems, if any, which could be considered potential sources of error or uncertainty for the results.