Earth Mapping Resources Initiative Protocols: Sampling solid hard-rock mine waste and perpetual mine water sources

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Abstract

Critical minerals are materials essential to the economic and national security of the United States with possible vulnerability to supply chain disruption (Nassar et al., 2020). Supporting the overarching goal to evaluate critical minerals nationwide, the mine waste characterization effort in the United States Geological Survey (USGS) Earth Mapping Resources Initiative (Earth MRI) has created a series of protocols to standardize sampling carried out under this effort by the participating state geological surveys and their cooperators. The protocols are based on published, reviewed methods, and are intended as methods to be deployed in the field as described here. The protocols include: (1) collecting and processing composite samples of mine and mill waste, including tailings, waste rock, gangue, heap leach piles, ore stockpiles, slag, or other mineralized/processed materials and (2) collecting and preserving water samples from perpetual or long-term mine water sources. The protocols also specify required information to be documented on field sheets and detail the collection of geospatial data. The analytical methods used by the USGS and USGS contract laboratories are described, including the data delivery pathway for USGS-derived data.

Introduction

The USGS Earth MRI initiative is an effort to modernize mapping of the surface and subsurface across multiple types of data including geologic, geophysical, geochemical, and topographical data. Areas across the United States with the potential to host both subsurface and surface deposits of critical mineral resources (‘focus areas’) have been identified by the USGS and their state geological survey collaborators (Hammarstrom, et al., 2023). Earth MRI focus areas are based on mineral systems, deposit types, and known and potential critical mineral commodities. The mineral systems classification links large mineral systems that may contain multiple deposit types to the mineral commodities associated with each deposit type (Hofstra and Kreiner, 2020). Earth MRI takes a mineral systems approach for prioritizing data collection efforts for both above ground and below ground critical mineral resources. One aspect of Earth MRI is to understand the distribution of critical minerals in above-ground mine waste.

The Earth MRI mine waste characterization effort collects compositional data to help identify mine waste sites that potentially contain critical mineral resources. The data can be used to estimate the critical mineral endowment of mine waste in the United States. Additionally, the data can be used to identify potential mineral hosts of critical minerals and provide a cursory evaluation of the environmental characteristics of the mine waste to help delineate potential reprocessing, environmental management, reclamation strategies, and other attendant costs. Identification of sites with critical mineral potential is the first step toward fostering economic development in conjunction with environmental remediation. Whether mine waste is a potential resource, an environmental liability, or both will depend on the geochemical and mineralogical characteristics of the waste. In addition, compositional characterization of mine waste may inform use of new technologies to reprocess mine waste more efficiently for extraction of critical minerals in the future. This information will be useful when assessing the total costs and benefits of reuse, recycling, reprocessing, reclamation, and restoration of ecosystem services. Evaluation of the future recoverability of critical minerals from mine waste is beyond the scope of this effort and will depend on a variety of factors including prevailing commodity prices, technological innovations, and financial incentives, among others. The goal is to develop a comprehensive and internally consistent national database of mine waste locations, volume and mass estimates, bulk geochemical composition, bulk mineralogical composition, and contained mineral commodities. To this end, this document describes the methods followed by participating state geological surveys and their cooperators to standardize sampling carried out by Earth MRI's mine waste characterization effort.

Scope

The scope of these protocols encompasses sampling of solid mine waste and large, perpetual mine-related water sources (for example, pit lakes and draining adits). Presented is an approach to sampling a variety of solid waste types, including tailings, waste rock, gangue, heap leach piles, ore stockpiles, slag, or other mineralized/processed materials. If other types of materials are present at the site (for example, efflorescent salts, secondary precipitates, or streambed sediments) and the opportunity to sample is available during the course of the study, please consult with USGS personnel associated with Earth MRI on methodologies for sampling. Guidance on field notes, geospatial data, and USGS geochemical analysis is also provided in this document. This document is intended to supplement the in-person training provided by the USGS to participating state geological surveys.

We recognize that many mine waste sites may be vertically heterogeneous. Vertical profile sampling in addition to composited surface samples may be considered. These protocols include an approach to sampling drill core, with the understanding that methodologies for drilling, trench sampling, or other vertical sampling techniques will not be discussed in detail as they will be highly site dependent.

Safety

Safety planning, including, but not limited to, job hazard analysis, selection of personal protective equipment (PPE), and appropriate safety training, is the responsibility of the state agency conducting the work. The USGS is not responsible for providing equipment, safety training, or evaluating site hazards and risks. Please work with your organization's safety officer to determine and complete the necessary safety requirements to perform the proposed work in a safe manner. Required PPE described in the sections below is provided as a guide for sample collection requirements. Additional PPE may be needed to conduct the work safely.

Protocols

Sampling approach for solids

Overview

Sampling of solid mine waste is complex due to the varied nature of source material, waste management approaches, climatological influence, and site accessibility. Sampling described in these protocols will be primarily focused on surficial material (0-10 cm depth; exceptions described below) using a statistically based, relatively rapid, composite approach based on Smith et al. (2000) and Naftz and Walton-Day (2016). Before sampling, the site should be divided into appropriate sample units, described in detail in the next section. Within each sample unit, the area will be subdivided into a grid or randomized distribution of least 30 subsample locations. For statistical rigor, a minimum of 30 subsample locations are required; more than 30 subsamples are acceptable. Subsamples of equal volume will be collected, combined into a single composite sample, and have a minimum combined dry weight of 1 kg (details described below). When a composite sample arrives at the USGS, it will be crushed and homogenized prior to submission for analysis.

Defining sample units, locations of subsamples, and depths of subsamples

The overall objective of designating sample units is to differentiate parts of the site that potentially could have different material composition or to divide a very large area into smaller units to obtain a series of composite samples that are more representative of site. The number of sample units will depend upon the size, topography, mine waste type, ore-processing history, geography of the site and other objective criteria, such as color. For example, if the tailings pile has discrete benches, each bench may be considered as a separate sample unit. Prior to going to the field, it is valuable to identify the features and boundaries to be sampled by recent satellite, aerial photography, or other imagery. The features may be subdivided into sample units if the feature is large and has topographical or other distinguishing attributes that indicate a change in composition or site management (for example, benches, discrete piles, tailings color). If the site is large with no clear distinguishing features, sample units of approximately 0.04-0.06 km^2 (10-15 acres) should be selected. If a pile has mixed types of waste or has areas that contain vastly different sizes of material, sample units can be drawn to reflect those differences. For example, if a pile has mixed fine-grained material and larger pieces (up to 30 cm) on the top of the pile, and boulder-sized rocks with no fine material around the base of the pile, the top of the pile may be considered a separate sample unit from the base. Different sampling methods can then be used to collect composite samples in each of the two sample units.

Site history is an important tool in understanding site features. For example, locations of pipes used to convey tailings, if available, can help guide distribution patterns on the landscape. Similarly, if the site went through multiple phases of ore processing, that information may be useful in interpreting different possible stratigraphy or topographical features at a site. Aerial imagery is incredibly helpful in understanding a site but is generally not sufficient to make final decisions about sampling approach. As such, site reconnaissance can be useful to more clearly identify the geography and topography of the features, and to determine if there are any coverings over the waste material.

Once sample units have been identified, at least 30 subsampling locations per sample unit should be selected using a systematic grid or randomized location scheme that adequately covers the sample unit. Subsample locations may be planned in advance of field work using geographic information system (GIS) tools, with any deviations from the plan noted in field notes or with a global positioning system (GPS) device. For example, if a particular preselected subsample location is inaccessible, an alternative may be selected on-site as close to the original location as possible. Pin flags or flagging tape are helpful for marking out subsample locations on-site prior to sample collection. If subsample locations are not selected in advance of the field work, pin flags or flagging tape should be laid out by the sampling team, visually confirming that the subsample locations adequately cover the sample unit before sampling begins, adjusting the locations and/or adding additional subsample locations as needed. A minimum of 30 subsamples are required, but more than 30 subsamples are acceptable. The subsample locations should be logged by GPS in the field if not pre-determined.

If a subsample location falls on a clearly unique or different feature within the sample unit, it should be collected and composited as planned (see also Grab Samples, below).

If the site has an obvious soil horizon, clay cap, engineered cover (for example, a geomembrane), or other natural or anthropogenic covering, the sampling procedure described below may need to be modified to collect the waste material below the cover as long as the sampling does not compromise the integrity of an engineered cover. Site history will be helpful in determining if an engineered cover is expected at the site. Negotiating with the landowners for sampling permission, especially if a cover is expected, is the responsibility of the state agency conducting the work. Once on site for sampling or during a reconnaissance visit, it is recommended that a test hole be dug (usually approximately 0.5 m deep but may vary depending on site characteristics) to visually determine if samples should be collected below the surface. For example, non-acid generating tailings may have vegetative growth and a surficial layer with roots and some soil formation. This soil layer is usually apparent in the test hole, and the sample collection depth should be below this layer for all subsamples, and the sample depth noted on the field sheets. As each site has a unique setting, please reach out to USGS personnel associated with Earth MRI to discuss variations in sampling design.

Grab samples

Within the sample allotment and budget, additional grab samples may be collected of any unusual or notable feature in addition to the composited sample. If the subsample location falls on a feature that is notable or different, it should be collected and composited as planned. Additional grab samples of that feature may then be collected. For example, if a pile has a distinct orange weathered layer on the surface with continuous primary black unweathered tailings material below, the composite sample should be collected below the weathered surface layer, but collecting a grab sample of the weathered orange surface layer at one or more subsampling locations would be beneficial. If available, 1-2 kg of grab sample material should be collected and submitted for analysis. However, if that mass is not available (for example, within a drill core, or a smaller distinct layer in tailings), a smaller amount of material may be collected, and fewer chemical analyses may be completed on that sample at the discretion of the USGS.

Protocols for composite sample collection of several mine waste material types

Tailings and fine-grained waste material

In general, tailings are the waste material from ore that has been processed to recover a concentrated form of the target commodity. Processing usually includes some form of grinding or milling of the ore, and as a result, tailings are usually fine grained (<2 mm). For most tailings, material on the surface that is >2 mm may be the result of cover or extraneous material deposition that should not be included in the composite sample. Sieving to <2 mm ensures that the sample collected is primarily the tailings material. Although unlikely in tailings piles, if the majority of the tailings have a grain size larger than 2 mm, the methodology described below for larger material types should be used. One composite sample will be collected for each sample unit, not including duplicate samples (described below) or additional grab samples.

Personal Protective Equipment (PPE):

- Nitrile gloves. It is possible to cover work gloves with nitrile gloves, if desired, but work gloves alone cannot be used. New nitrile gloves should be donned for each sample unit to prevent cross-contamination.
- Additional PPE may be required (for example, masks, eye protection, clothing covering) depending on the site conditions and hazards (see Safety, above).

Equipment:

- Shovel
- Trowel, small shovel, or incremental sampler (stainless steel or plastic are necessary to prevent metal contamination)
- 5-gallon plastic bucket

- Large (1 gallon) plastic bags or other sealable container
- Labels and permanent markers
- 2 mm plastic or stainless-steel sieve
- Flagging tape and/or pin flags to mark subsample locations. Consider the choice of color so that the flags stand out in the sampling landscape.
- Wire brush to remove particles from sieve as needed in between samples
- Deionized (DI) water (or equivalent) and a squirt bottle for cleaning equipment. If DI water is not available, distilled water can be substituted. Tap water should not be used.
- Paper towels or kimwipes

Sampling tools, sieve, and buckets should be rinsed with DI water and air dried prior to sample collection.

Subsample depth and amount collected: Subsamples should be collected from the upper layer of the tailings pile, 0-5 cm deep, unless it is necessary to sample below a soil layer, cap, oxidized layer, hardpan or crust. A test hole should be dug prior to first subsample collection to determine whether there is a soil, cap, or oxidized layer on the surface of the tailings pile. Although aerial imagery and site history are extremely helpful for guiding sampling strategy, the best way of determining if there is a layer on top of the tailings is to dig to a depth of 0.25-1 m and observe any variation in color, particle size, plant roots (if present), moisture content, and/or other properties. If there is an obvious soil layer or cap on top of the tailings, then subsamples should be collected at the same depth below the anomalous surface layer. Evidence of weathering (often indicated by a color change or hardpan layer) should be noted in the field sheet. The training provided by the USGS can help identify these types of situations and inform the sampling strategy on a site-by-site basis.

Each subsample within a sample unit should be collected to the same depth and volume using the same equipment. The mass should be at least approximately 50 g per subsample. The amount collected for each subsample can be approximated using the sampling equipment, a bag, or other container, as long as the same amount of sample collected is consistent at each subsample location. For example, if using a trowel to collect the subsample, the trowel should be filled to approximately the same amount of sample at each location. If using a plastic bag or container, the fill level should be marked with a permanent marker on the bag or container and filled to that level at each location. The method used may depend on the wetness, particle size, or other factors specific to the site material. It is not necessary to weigh each subsample. The total mass of the sieved composite sample after all of the 30 or more subsamples have been combined should be at least 1-2 kg dry weight.

Compositing subsamples and sieving: Composited samples should be sieved to <2 mm in the field or after being transported to a laboratory setting. If possible, it is recommended that subsamples be sieved in the field during collection. As each subsample is collected, it can be sieved directly into the bucket; each subsample is sieved and sequentially added to the same bucket, which becomes the composite sample. Tailings materials that are damp are usually able to be sieved, unless the sample has very high clay content.

If the sample cannot be sieved in the field (for example, very high clay content), the bulk material from each subsample can be directly added to the bucket for sieving at a later time. If there are large particles (>1 cm) in the subsample, the particles should be removed. Similarly, large items (>1 cm) of manufactured material (for example, bolts, screws, rebar) should be removed and recorded in field notes. If the material has a large amount of coarse (>2 mm) material, additional mass may need to be sampled at every subsample location to accommodate the amount of >2 mm mass discarded during sieving.

If the samples have a high clay content, sieving will be challenging in the field and in the laboratory, as clay can be sticky when wet and harden into large aggregates upon drying. In this case, please contact USGS personnel associated with Earth MRI for more guidance, and the USGS may be able to assist with sample preparation.

If tailings samples are wet upon collection, the samples should be air dried before submitting to USGS sample control. If sieving is occurring in a laboratory setting after collection, any particle agglomerates that have formed upon drying a wet sample should be disaggregated before sieving.

The dry, sieved composite sample should be at least 1-2 kg, dry weight. The >2 mm fraction will not be submitted or analyzed and can be discarded. Once the composite sample has been sieved, the material can be transferred to a plastic bag, sealed and labeled. Double- or triple-bagging is highly recommended prior to shipping to prevent loss of material during transit.

Detailed notes about soil/surface anomalies, subsample depth, volume, sieving and other decisions for each sample unit should be made in the field sheets. Sample containers should be labeled in the field. If the composite sample needs to be sieved in the laboratory, a note should be made in the field sheet and on the sample container (for example, “unsieved bulk composite sample”) in addition to the label with the site name, date, and other information. Any deviations from the described methods should be noted in the field sheet.

Material containing <2 mm particles mixed with pieces larger than 2 mm, but generally smaller than about 30 cm

It is not uncommon to have mine waste that is a mixture of fine material and larger pieces, such as in an ore stockpile that has had some initial bulk crushing but was never milled. In these piles, both the <2 mm fraction and the >2 mm fraction are important to collect and analyze. Two composite samples will be collected at each sample unit, not including duplicates (described below) and additional grab samples. The approach consists of sieving the material to <2 mm and retaining the >2 mm fraction, with additional processing required for larger pieces of material, as needed, to prevent a single large piece from biasing the >2 mm fraction. The two fractions will provide end-member compositions for the overall pile.

Personal Protective Equipment (PPE):

- Nitrile gloves. It is possible to cover work gloves with nitrile gloves, if desired, but work gloves alone cannot be used. New nitrile gloves should be donned for each sample unit to prevent cross-contamination.
- Eye protection. Safety glasses are recommended especially if the material is large enough to require rock chipping.
- Additional PPE may be required (for example, masks, clothing covering) depending on the site conditions and hazards (see Safety, above).

Equipment:

- Shovel
- Rock hammer, small sledge, and/or pickaxe
- Trowel, small shovel, or incremental sampler (stainless steel or plastic are necessary to prevent metal contamination)
- 5-gallon plastic buckets (2 per sample unit: one for the <2mm fraction and one for the >2mm fraction)
- Large (1 gallon) plastic bags or other spill-proof container
- Labels and permanent markers
- 2 mm plastic or stainless-steel sieve
- Flagging tape and/or pin flags to mark subsample locations. Consider the choice of color so that the flags stand out in the sampling landscape.
- Wire brush to remove particles from sieve
- Deionized (DI) water (or equivalent) and a squirt bottle for cleaning equipment. If DI water is not available, distilled water can be substituted. Tap water should not be used.
- Paper towels or kimwipes

Sampling tools, sieve, and buckets should be rinsed with DI water and air dried prior to sample collection.

Subsample depth and amount collected: If the material allows, a test hole will yield valuable information about material size and distribution. If some of the material is larger than 10-15 cm in diameter or length, it may be challenging to dig and a surficial sampling approach will suffice. However, it is important to confirm, if possible, that the surficial material is not a cover on top of the mine waste.

Each subsample within a sample unit should be collected to the same depth and volume using the same equipment. The amount collected for each subsample can be approximated using the sampling equipment, a bag, or other container, as long as the same amount of sample is consistent at each subsample location. For this material type, a shovel or similarly sized container is usually a reasonable tool to estimate the sample amount, unless the material is mainly fine-grained, in which case a trowel can be used. It is not necessary to weigh each subsample. Enough material should be collected at each subsample to yield about 50 g at each subsample location for both the <2 mm and >2 mm fractions. If the material is mainly fine-grained, this protocol will be functionally similar to the tailings protocol above, with the exception of retaining the >2 mm fraction. If the material has a larger proportion of >2 mm material, assure the subsample is large enough to collect about 50 g of <2 mm material at most locations. The total mass of each composite sample (< 2 mm and >2 mm) after all 30 or more subsamples have been combined should be at least 1-2 kg, dry weight.

Compositing subsamples, sieving, and processing >2 mm fraction: The <2 mm and >2 mm fractions of the sample will be collected in two separate buckets. If possible, each subsample should be sieved to <2 mm directly into a bucket in the field. The material that does not pass through the 2 mm sieve should be retained and processed as follows:

- If most of the >2 mm fraction retained on the sieve is less than approximately 4 cm in length or diameter and is about 50 g worth of material, it can be placed directly into the second bucket. If this fraction is substantially more than approximately 50 g of material, a ~50 g randomized subset of material should be selected and placed into the second bucket, and the remainder discarded. It is important to not bias the selection toward items of a particular size or color; the subset of material should be representative of the bulk >2 mm material.
- If there are pieces larger than approximately 4 cm, they should be removed from the shovel directly and placed aside. Large pieces of material can bias the overall composition of a composite sample and need to be reduced in size to be included in the sample. A random selection of large pieces should be chosen, with care taken to not bias the selection toward items of a particular size or color. These large pieces should then be broken with a sledge or rock hammer and a single chip (~4 cm in length or diameter) collected into the second bucket.
- If there is a mix of <4 cm and >4 cm pieces in the >2 mm fraction, then a combination of the two processes should be used. For example, a random selection of <4 cm pieces should be placed in the second bucket, along with ~4 cm chipped samples from the larger pieces.
- Subsamples may exhibit different distributions of large and fine material within a single sample unit. Continue to sample at all locations using the same approach, even if it results in <50 g material for a size fraction at a single subsample location. For example, most subsample locations may have a roughly equal distribution of <2 mm and >2 mm fractions, but one subsample location only has 20 cm rocks and no fine-grained material. At this location, collect the rock chips and no fine-grained material. The composite approach normalizes over the individual subsample location variations to collect an average composition across the entire sample unit.

Each subsample should be collected as described above, resulting in two buckets: one bucket with <2 mm sieved material, and one bucket with >2 mm material including rock chips. Each composite sample (<2 mm and >2 mm) should be at least 1-2 kg, dry weight. The composite sample from each bucket can be transferred to two different plastic bags, sealed, and labeled. Double- or triple-bagging is highly recommended prior to shipping to prevent loss of material during transit.

Large material predominantly >30 cm

Some waste material, such as waste rock, may have very little fine material and only large pieces that can range from several kg to many hundreds of kg. In these cases, a <2 mm fraction should not be collected, and we present a method to subsample these large items to collect a representative composite sample.

Personal Protective Equipment (PPE):

- Nitrile gloves. It is possible to cover work gloves with nitrile gloves, if desired, but work gloves alone cannot be used. New nitrile gloves should be donned for each sample unit to prevent cross-contamination.
- Eye protection. Safety glasses are strongly encouraged because the protocol requires rock chipping.
- Additional PPE may be required (for example, masks, clothing covering) depending on the site conditions and hazards (see safety, above).

Equipment:

- Rock hammer, small sledge, and/or pickaxe
- 5-gallon plastic bucket
- Large (1 gallon) plastic bags or other spill-proof container
- Labels and permanent markers
- Flagging tape and/or pin flags to mark subsample locations. Consider the choice of color so that the flags stand out in the sampling landscape.
- Deionized (DI) water (or equivalent) and a squirt bottle for cleaning equipment. If DI water is not available, distilled water can be substituted. Tap water should not be used.
- Paper towels or kimwipes

Sampling tools and buckets should be rinsed with DI water and air dried prior to sample collection.

Subsampling approach: With this material type, the subsample points likely will fall on large rocks or boulders. To subsample a large rock, use a rock hammer, sledge, or other tool to chip off 3-5 randomly selected pieces of material approximately 4 cm from the surface of each rock. These pieces should be placed directly into the bucket, accumulating rock chips across all of the subsample locations. The composite sample will be the mixed rock chips in the bucket from at least 30 subsample locations and should be at least 1-2 kg dry weight. The composite sample can be transferred to a plastic bag, sealed, and labeled. Double- or triple-bagging is highly recommended prior to shipping to prevent loss of material during transit.

Drill cores

Drilling is not required for site characterization, but if equipment and budget allow, is encouraged because it allows for samples to be collected across the third dimension of a pile. The details of the best equipment, techniques, and PPE for drilling at the site will be at the discretion of the state agency conducting the work. Tailings and other fine-grained mine waste are good candidate materials for drilling, resulting in a poorly consolidated core with some larger clasts possibly present. The methods described below assume the core is relatively unconsolidated and does not need a rock saw to split or collect samples. If the core does not meet this description, a discussion with USGS personnel associated with Earth MRI may be warranted.

Equipment:

- Trowel and/or scoop (stainless steel or plastic are necessary to prevent metal contamination)
- Rock hammer or other tool to split clasts as needed
- Plastic buckets or other containers for the composited samples
- Large (1 gallon) plastic bags or other spill-proof container
- Labels and permanent markers
- Tape measure for measuring sample unit intervals
- Deionized (DI) water (or equivalent) and a squirt bottle for cleaning equipment. If DI water is not available, distilled water can be substituted.
- Paper towels or kimwipes

Sampling tools and buckets should be rinsed with DI water and air dried prior to sample collection.

Determining sample intervals (sample units) within a core: If core logs are available, it is recommended that they be reviewed to identify where stratigraphic breaks occur in the core and how frequently they occur. Laying the core out to visually identify the stratigraphic breaks is also suggested. If the material is homogeneous, then dividing the core into equal sections over the entire core depth is an option depending on how many samples per core is reasonable for the budget. It is more likely, however, that there are apparent heterogeneities in the core. These heterogeneities or stratigraphic beaks can define sample units within the core such that a sample unit includes depths in between the stratigraphic breaks. Samples will be composited across a sample unit defined within the core (described below), so that composition is not dominated by only collecting individual or interesting layers within the core. Distinct or unusual layers may be used to separate sample units but should be included in the composite sample. Depending on the stratigraphy of the core, sample units may be of variable lengths. In sample sheets, note the depths/location in the core where sample units begin and end after laying out the entire core. Each sample unit will result in one composite sample.

In the case of highly variable or closely spaced breaks, some judgement will need to be applied to balance the need to define sample units for compositing and capturing every heterogeneity presented in the cores. In addition to composite samples, grab samples are encouraged, particularly if there are distinct layers that are different from the surrounding material. The grab samples can be collected after the core is split and the composite sample collected. This ensures that the composite sample includes the distinct layers while the composition of the layers may also be captured individually in grab samples. The balance between the number of composite samples and grab samples will depend upon the overall scope of the project, including the number of drill cores, other samples collected (for example, surface composite samples), and sample budget.

Collecting composite samples: Depending upon the diameter of the core, splitting the core vertically in half or quarters will likely be necessary. If there is a rock or clast in the core, split it with a rock hammer or similar tool. The composite sample should be collected by taking the split material in a sample unit (within the determined stratigraphic interval) and combining it in a bucket. The composite sample should be approximately 1-2 kg, dry weight. The sample material should be transferred to a plastic bag, sealed and labeled. Double- or triple-bagging is highly recommended prior to shipping to prevent loss of material during transit. Grab samples may be collected from the uncomposited split section of the core.

Quality assurance and quality control (QA/QC) and equipment cleaning for all sample types

Duplicates and blanks

Field duplicate samples give an important indicator of overall sampling variability at a site. A duplicate sample should be collected at a frequency of one per 10 samples. If fewer than 10 samples are collected at a site, then one sample unit should be selected for a duplicate sample collection. A duplicate sample should go through the same subsample collection, composite, and sieving process and labeled as a separate sample with a unique ID. Subsamples for the duplicate sample can be collected nearby (within ~1 m radius) and use the same GPS location of the original subsample location but should not be collected from the same hole as the original subsample.

For drill cores, a duplicate sample should be collected from a sample unit within a core at a frequency of one in 10 samples. Duplicates should be collected by compositing a separate split of the core. If grab samples are also planned to be collected from the core in that section, the core in that sample unit should be vertically split into thirds or quarters so material is not excluded from the composite sample or duplicate sample.

A process blank is optional but recommended. A blank consists of a known material, typically clean quartz from a commercial supplier, that is put through the sampling process using all of the equipment. For example, if a trowel is being used to collect the tailings subsamples, the clean trowel will be used to scoop the blank material through the sieve into a bucket and bagged as if it were a tailings sample. If you are interested in including a blank, please reach out to the

USGS Earth MRI personnel and we will supply the quartz blank material and discuss safety considerations when working with quartz.

Equipment cleaning in between sample units

The trowel/shovel/sampler, sieves, and buckets should be cleaned before next sample collection. They should be wiped with a clean rag, paper towel, or lab wipe, then care should be taken to remove any particles stuck within the sieve mesh before washing. The wire brush may be necessary to remove particles from the sieve mesh. Lastly, equipment should be rinsed with DI water at least 3 times, and completely air dried before next sample collection. CThe wire brush may be used to clean the sieve in between subsample locations if the mesh is substantially occluded (for example, with clay).

Sample labeling, handling, and storage for all sample types

Sieved samples should be secured in a plastic bag or other spill-proof container and labeled with indelible ink. Double- or triple-bagging is recommended to prevent loss of sample during transport. The sample label should contain a unique site and sample unit ID, date of collection and size fraction (for example, <2 mm) once sieved. Including a project ID that indicates the program (Earth MRI-Mine Waste Characterization) and state is also highly recommended. Duplicate samples should be labeled with a unique ID. Unique IDs will need to be tailored for the particular site and sample type, but we suggest using a consistent format. For example, if the sample is from a site called “Example Tailings Site” in state YY and is a composite sample from sample unit 1 collected on November 1, 2022 at 15:00, the unique sample ID could be: “22_ETS_SU1_composite”, with details about the exact date and time recorded in the field sheet and on the label. A duplicate sample could be labeled “22_ETS_SU1_composite_dup” to differentiate it from the first sample. If the mine waste material is a mix of fine-grained and larger materials, resulting in two composite samples from a single sample unit, additional information needs to be added to the label to identify the sample size fraction (for example, add “<2 mm” or “>2 mm” on the sample label; see figure 1).

Figure 1. An example sample label.

22_ETS_SU1_composite
1 Nov 2022 15:00
<2 mm
EMRI-MWC-YY

Holding temperature of samples does not have to be controlled. Samples should be air-dried, inventoried, and submitted to USGS Sample Control (see section on Sample Submission below).

Extra equipment for sampling solids

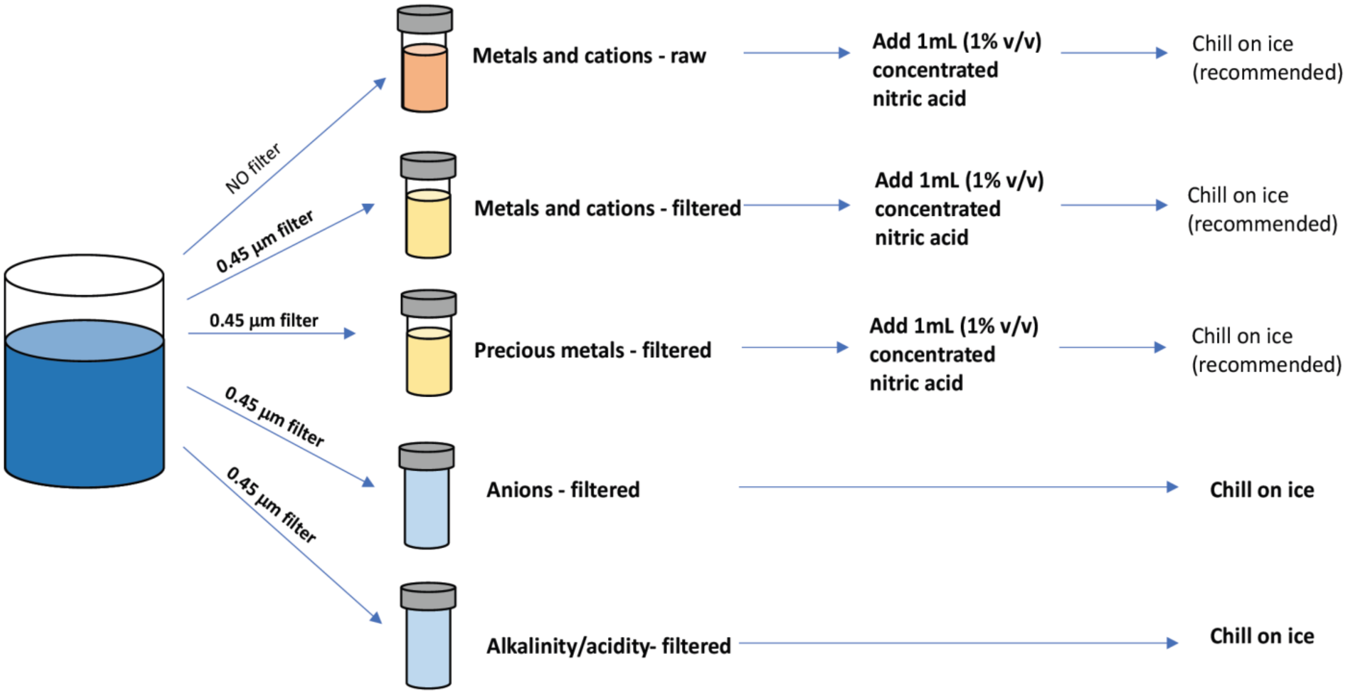
Even with the best planning possible, it is almost always necessary to have extra supplies on hand. We recommend packing extra DI water, buckets, and other supplies.

Water Sample Collection, Preservation, and Measurement of Field Parameters and Flow

Overview

Methods for water sample collection and preservation are derived from the USGS National Field Manual for the Collection of Water-Quality Data (NFM; Wilde, 2011), specifically chapters A1 (USGS, 2018), A2 (Wilde, et al., 2014), A3 (Wilde, 2003), A4 (USGS, 2006), A5 (USGS, 2002), and A6 (Nordstrom and Wilde, 2005; USGS, 2019; USGS, 2020; USGS, 2021; USGS, 2023; USGS, 2024). An overview of the sample collection and preservation methods is presented in Figure 1. Depending on the type of site sampled (for example, pit lake, or adit drainage), additional equipment may be needed to collect the water sample (for example, boat, sampling pole,or other equipment). Generally, water will be extracted via a peristaltic pump and through a filtration apparatus or directly into a bottle, although alternate methods such as syringe filtration are acceptable. When water samples are collected, field parameters (pH, temperature (T), specific conductance (SC); optionally dissolved oxygen (DO) and oxidation-reduction potential (ORP)) should also be measured.

Figure 1. Conceptual flow chart of water sample collection and preservation.



Equipment and preparation

PPE

- Clean nitrile or similar laboratory-grade gloves should be worn when handling equipment that comes in contact with sample water and during sample and field parameter collection.
- Note about sunscreen: personnel should be aware that some sunscreens contain Zn and/or Ti oxides, and should be avoided if possible during water sampling. If not avoidable, personnel should be extra careful about minimizing any possible direct contact with equipment without clean gloves.
- Safety glasses
- Other PPE may be necessary depending on sample collection method (for example, if collecting via boat) and site conditions (for example, masks, eye protection, clothing covering); see Safety section, above.

Bottle sets

Each sample collected will be distributed into a set of 5 bottles:

- Metals and cations: Two 125 mL acid-washed plastic bottles
- Precious metals: One 125 mL acid-washed plastic bottle
- Anions: One 125 mL deionized water-rinsed plastic bottle (**NOT** acid washed)
- Alkalinity/Acidity: One 125 mL deionized water-rinsed plastic bottle (**NOT** acid washed)

Table 1. Overview of bottles, preparation, and preservation for water samples. Filtration pore size is 0.45 μm.

Analysis	Bottle	Preparation	Filtration	Preservation	Label suffix
Metals and cations, raw	125 mL plastic bottle	Acid wash	None	1% v/v concentrated nitric acid	-RA
Metals and cations, filtered	125 mL plastic bottle	Acid wash	Filter (0.45 µm)	1% v/v concentrated nitric acid	-FA
Precious metals	125 mL plastic bottle	Acid wash	Filter (0.45 µm)	1% v/v concentrated nitric acid	-FA
Anions	125 mL plastic bottle	Deionized water rinse	Filter (0.45 µm)	Chill at 4 °C	-FU
Alkalinity/acidity	125 mL plastic bottle	Deionized water rinse	Filter (0.45 µm)	Chill at 4 °C	-FALK

Bottles should be labeled with waterproof labels (recommended) or lab tape. If labeling with tape, the tape should be wrapped around the entire circumference of the bottle and secured by overlapping to prevent detachment. Labels should be printed and/or written in indelible ink. Each bottle must be uniquely labeled with the site name, date and time of collection, the analysis, and associated preservation. Including a project ID that indicates the program (Earth MRI-Mine Waste Characterization) and state abbreviation is also highly recommended. Abbreviations for preservation should be added to the sample name according to Table 1 (for example, unfiltered metals/cations should be labeled with the suffix “-RA” for “raw, acidified”; filtered metals/cations and precious metals should be labeled with the suffix “-FA” for “filtered, acidified”; filtered anions should be labeled with the suffix “-FU” for “filtered, unacidified”; filtered alkalinity splits should be labeled with the suffix “-FALK” for “filtered, alkalinity”).

Figure 2. Example label for a hypothetical sample collected at the “Example Water Site” from the “Big Pit Lake” in State YY on November 1, 2022, at 15:00 hours, the bottle for filtered metals and cations.

22_EWS_BPL_001-FA
1 Nov 2022 15:00
EMRI-MWC-YY
Metals and Cations

or

EWS_BPL01_20220111_1500-FA
1 Nov 2022 15:00
EMRI-MWC-YY
Metals and Cations

In the first example label in Figure 2, the “_001” was added in the event that multiple samples are collected from the same site on different days (time series); the second sample could be indexed to “_002”. In the second examplelabel in Figure 2, the time and date are incorporated into the unique ID; however, take care to prevent typographical errors in long strings of numbers such as a date when writing the labels. The abbreviation for a specific location (in this case, BPL) may depend on where and how many samples are collected. If sampling multiple locations at a single large feature, “BPL01” may be used to delineate specific locations. In all cases, details about the site, sample location, date, time, etc., should be clearly described in the field sheet notes.

Bottle preparation

Acid washing bottles for cation/metal sample splits

All metals/cations and precious metals bottles should be acid washed prior to use. Some laboratory supply companies have the option to purchase pre-cleaned bottles, but this is not required as long as the bottles can be sufficiently cleaned. If using a water collection container, it also should be acid washed prior to use.

If acid washing bottles, the acid bath should be a 10-20% reagent grade nitric or hydrochloric acid solution, and the bottles and caps should be soaked for at least 12 hours. The bottles should be well-rinsed at least 3 times with deionized water (DI water, 18 MΩ preferred, or similar). The bottles should be air dried in a clean environment (for example, laminar flow hood). The acid bath should be made fresh every 6 months.

Deionized (DI) water rinse for anion and alkalinity/acidity sample splits

Anion and alkalinity/acidity bottles and caps should be soaked overnight in DI water prior to use. Some laboratory supply companies have the option to purchase pre-cleaned bottles, but this is not required as long as the bottles can be sufficiently cleaned. Bottles for anion and alkalinity/acidity sample splits should not be acid washed.

Cleaning pumps and tubing

Peristaltic pumps are generally the best option for collecting water samples, as long as the height of the pump above the water body does not exceed the hydraulic head rating of the pump. If the water needs to be pumped to a height that exceeds the pump rating, then an alternate pump will need to be considered. Tubing will need to be acquired that is compatible with the pump and pump head used. The tubing should be rinsed with DI water and air dried completely prior to sampling. If feasible, each site should have its own dedicated tubing to prevent carryover between sites. However, if the tubing needs to be reused, it is recommended that it be rinsed with DI water in the field, if possible, or thoroughly rinsed with sample water before collecting the sample. Rinsing with sample water should not be done if sampling water with low concentrations immediately following water with high concentrations, or if the relative concentrations cannot be determined.

Filters

Preferred filters are clean, unused 0.45 μm pore size, high-capacity capsule filters, although other 0.45 μm filtration systems are acceptable (for example, plate filters, syringe and syringe filters). Filters should be prepared according to the manufacturer’s instructions if applicable. The filtration type and membrane material should be noted in the field sheet (see below).

Water collection containers

Depending on the site, extra containers to collect raw sample for filtration and/or splitting into bottles may be required. Containers may be needed if water cannot be directly pumped from the source. The container(s) may be a carboy, a large bottle, or other clean (acid-washed) container that can hold enough sample to rinse equipment, bottles (as needed), and collect sample splits. The volume needed will depend upon the type of equipment being used; for example, if a capsule filter is being used, a minimum of 2.5-3 L water collection container is recommended so that the filter can be rinsed with at least 1L of sample before sample splits are collected, per manufacturer’s instructions. The water collection container(s) should be rinsed three times with the sample before filling. A separate, non-acid washed container for field parameters should be rinsed and filled at the same time, if *in situ* measurements are not possible.

Additionally, access to water may require a collection mechanism such as a dipper sampler (for example, a “bottle on a stick”) which allows water to be sampled from a distance of up to 2-3 m. This device is useful at treatment plants, adits, ponds, and pit lakes where there may not be direct easy access (for example, water tap). There are commercially available dipper samplers, but home-made samplers are also acceptable. The dipper container should be clean (acid washed) and changed in between sites. Reconnaissance and/or discussion with personnel familiar with the site may be helpful to determine if a dipper or other sampling devices are necessary.

Preservation

- Preservation for -FU and -FALK samples
    - Cooler and ice in the field and during shipping
    - Refrigerator in the laboratory
- Field preservation for -FA samples:
    - High purity nitric acid (HNO_3), concentrated (16M) and
    - Distribution system:
        - pipette, clean pipette tips, bottle for acid (teflon preferred), or
        - dripper bottle calibrated in the laboratory for how many drops approximately equals mL of acid, teflon preferred.
- OR pre-washed bottles with high purity nitric acid preservative added by manufacturer for -FA and -RA samples.

Water for Blanks

Deionized water (DI water, 18MΩ preferred) should be brought into the field for a field blank (see below). The volume of water will depend on the length of tubing and the filtration system, but it should be sufficient to replicate the entire water collection process with DI water, including rinses and filling a complete bottle set.

Extra equipment for water sampling

Even with the best planning possible, it is almost always necessary to have extra supplies on hand. We recommend packing at least 10% extra bottle sets, filters, preservation materials (if not using prefilled bottles), DI water, water collection containers, and other supplies. If the water has a lot of particulates, additional filters may be required. For example, if using 33 mm diameter syringe filters, 5-10 filters per sample may be required. One high-capacity capsule filter is usually sufficient per site, even with high particulate loads.

Equipment reuse

Some equipment used for sampling should not be reused. Bottles used in bottle sets are single use and will not be returned. Similarly, all filters are single use and should not be used at multiple sites or on multiple dates. If using a pipette to distribute acid into bottles requiring preservation, a single tip can be used to distribute acid into multiple bottles at a single site as long as the tip does not touch the sample water or a dirty surface, but the pipette tips should not be reused in between sites.

Some equipment may be reused if cleaned in between sites. Items in this category include pump tubing and collection containers. If possible, tubing and collection containers that are dedicated to a site are preferable, but thorough DI water and sample rinses in between sites may be used if necessary. Extra DI water should be brought to the field if rinsing in between sites is anticipated.

Field parameters

If possible, it is best to measure field parameters *in situ* (electrodes placed directly into water source), but if it is not feasible to do so, a flow-through cell, bottle, or flask may be used. If measuring *in situ*, place the probes downstream from the where the water sample is being collected or collect water samples immediately before or after measuring field parameters to prevent contamination. A meter or meters will be needed to measure the output from each electrode and perform the calibrations. If carefully selected, the same meter may be used for pH, T, SC, ORP and DO (if probe used). Alternatively, a sonde with the ability to read the output and perform calibrations may be used. We recommend that you test the electrodes/meters in the office or lab prior to conducting field work. We also recommend (but not require) that you bring spare electrodes to the field, as it is not uncommon for mine waters to degrade electrode performance. ORP and DO are optional parameters but are recommended if the equipment is available. Below are the specifics of the equipment and supplies needed to conduct the various measurements

- pH:
    - pH electrode with appropriate outer filling solution, if required. A triode (with temperature) or the ability to measure temperature simultaneously with pH on the same meter (for example, via thermistor or specific conductance probe) allows for appropriate temperature compensation. An electrode with guards around the glass membrane is recommended but not required.
    - Meter to display results
    - Calibration buffers (set of at least 3, bracketing the pH of the water to be measured: 1.68, 4.01, 7.00, 10.01. NIST traceable preferred)
    - QA check sample (a separate aliquot of a buffer or other solution of known pH)
    - Flask or flow-through cell
    - DI water
    - Lab tissues
- Temperature (T)
    - Thermistor or liquid-in-glass thermometer (non-mercury); specific conductance and pH probes typically have a thermistor included and this may be used to measure temperature
    - Meter to display results
    - Flask or flow-through cell
    - DI water
    - Lab tissues
- Specific conductance (SC) (also known as conductivity or electrical conductance)
    - Conductivity probe (typically a 1 cm cell width)
    - Meter to display results
    - Calibration standards (typically 500 μS/cm, 1,413 μS/cm, or 12,900 μS/cm, whichever is closest to, and higher than the water being measured; 1,413 μS/cm is a typical calibration standard)
    - QA check sample (a solution of known SC, similar to the expected concentration of water to be measured; may be a separate aliquot of a calibration standard)
    - Flask or flow-through cell
    - DI water
    - Lab tissues

- ***OPTIONAL***: Oxidation-reduction Potential (ORP)
    - Platinum electrode with associated filling solution
    - Meter to display results
    - ORP check standard (for example Zobell's solution or other manufacturer's standard)
    - Flask or flow-through cell
    - DI water
    - Lab tissues
- ***OPTIONAL***: Dissolved oxygen (DO)
    - DO kit using Rhodazine D or Indigo Carmine colorimetric reagents.
    - Waste disposal container
    - DI water
    - Lab tissues
    - Alternative: DO meter and probe (see method section below)

Water collection protocol

Rinsing with sample: Water should be pumped through the tubing without collecting a sample to sample-rinse the tubing; the amount may depend on the length of the tubing used but should be approximately one liter (1 L). Similarly, the filter should be rinsed according to the manufacturer's instructions (for example, at least 1 L for capsule filters). Please take the time to read the manufacturer's guidance for specific filter requirements. The tubing and filter can be rinsed simultaneously.

Bottles should be rinsed three times with sample water before collecting the sample, unless the bottles are pre-filled with preservative. In that case, the bottle should be filled with sample directly without rinsing.

Filtration

For the raw metals/cations sample, no filter should be applied when collecting the sample. All other samples should go through a 0.45 μm filter before collection. Bottles should be filled to the shoulder of the bottle (~100 mL), except alkalinity/acidity, which should be filled to top, leaving minimal headspace in the bottle.

Preservation

Metals analysis: For raw and filtered metals/cations and precious metals samples, the sample should be acidified in the field to 1 % volume/volume nitric acid. For example, if filled to the shoulder of a 125 mL bottle, it contains approximately 100 mL of sample, and 1 mL of concentrated nitric acid should be added to the bottle. Wear safety goggles and gloves while acidifying and shake the bottle after capping to mix.

Anions and alkalinity/acidity: Filled bottles should be stored on ice in the field. Ice should be kept in sealable plastic bags to prevent melted ice from contaminating the samples.

QA/QC: Duplicates and blanks

For each sampling event (date), at least one DI water field blank should be collected. The entire sample collection protocol should be followed with DI water, including rinses and a complete set of sample bottles. A duplicate sample set should be collected at least once per sampling trip or one per every 20 sample sites, if more than 20 sample sites are collected in a single sampling event.

Sample handling, storage and shipping

Each bottle should be clearly labeled as described above. Samples of a single analytical type (for example, alkalinity or precious metals) should be grouped into a sealable bag; samples of mixed analytical types are not acceptable. Samples should be stored with caps tightly closed to prevent leakage and in plastic bags to prevent melted ice or dirt from contaminating the samples. Multiple samples may be stored in a single plastic bag as long as they are of a single analytical type, but the bag should be sealed. Double-bagging is recommended.

Anion and alkalinity/acidity samples should be kept chilled in the field, during shipment, and when stored in the laboratory. Metals/cations and precious metals samples may be chilled, but it is not required; it is best to not let the samples get excessively hot. No samples should be frozen at any time.

Samples should be inventoried, and samples submitted to USGS Sample Control (see section on sample submission below).

Flow and discharge measurements

If water sampled is flowing (for example, from an adit), the flow or discharge should be measured or estimated. Determine whether the site manager has the ability to measure the flow (for example, a gage, valve, or permanent weir), and if so, that flow data may be used. If no site discharge data are available, various measurement techniques may be used depending on the volume of flow and site characteristics (EPA, 2001). For example, a weir (permanent or temporary) or flume may be used for lower flow systems, whereas direct flow velocity measurements (for example, with an anemometer, propeller, or Doppler meter) may be needed for larger flows. Tracer techniques with salts or dyes can also be used. Volumetric flow measurements, where the time taken to fill a specific volume three times, are also acceptable. The choice of method will depend on expected flow, site conditions, channel geometry, availability of equipment, and access. The selection of methods to measure flow and discharge can be complex (EPA, 2001) . If no flow data can be obtained, a visual estimate should be made. Regardless of the technique used, details should be documented in the field sheet.

Load calculations

Loading is a useful expression of how much of a particular element is flowing past a point in space as a function of time; loading incorporates both concentration and discharge information for a flowing water source. Instantaneous load is calculated for a location by multiplying discharge by constituent concentration. Units are typically expressed in g (or kg) per day for each element reported. The loads should be calculated and included in the final report.

Field parameters

In all cases, operational specifics unique to the electrodes/meters or sondes being used may be needed in addition to the method provided below to complete successful analysis of field parameters.

pH

pH should be measured in the field, *in situ* or in a flask or beaker filled with sample as close to ambient conditions as possible. If it is not possible to measure pH in the field, an additional sample split may be collected, stored in a clean bottle, filled to the brim with sample water, and chilled during transport and storage at the lab. Measurements must be made within 48 hours, and this deviation in procedure noted in the field sheet.

Because pH is temperature dependent, it is important to measure temperature simultaneously with pH and to calibrate at ambient temperature for automatic temperature compensation.

1. Attach the electrode to the meter (if not already in a sonde) and prepare electrode according to manufacturer's instructions.
2. When moving electrode between buffers and samples, the electrode should be rinsed with DI water and blotted dry with a lab tissue to prevent cross contamination.
3. Calibrate on 2 or 3 buffers that bracket the pH of the water being sampled. The calibration buffers should be as close to the same T as the sample as possible. Calibration slope, T, and buffers should be recorded on the field sheet. The slope should be between 92% and 102%. If it is not, the calibration should be repeated, or a different electrode used. The lot numbers and expiration dates of the buffers should be noted on the field sheet.
4. Check the pH of a QA check sample (for example, a different aliquot of a buffer or a solution with known pH). It should be within 0.05 units of its accepted value. Record this result in the field sheet. If the QA check fails, then the calibration needs to be redone.
5. Measure the pH of the sample and record the value in the field sheet.
6. Up to 10 samples may be measured before the QA check sample needs to be remeasured, as long as less than 2 hours have passed, and the pH meter and electrode have not been moved to a new location. If either of those conditions are not met, then steps 4 and 5 should be repeated. It is acceptable to measure the QA check sample after every sample if desired.
7. At the end of the sampling day, a last QA check sample should be analyzed according to step 4 and recorded on the last field sheet.
8. Store the electrode according to the manufacturer's instructions.

If the pH of the water falls outside of the buffers used for calibration, the data will need to be qualified, and the situation should be noted in the field sheets.

Specific conductance (SC)

Because SC is highly temperature dependent, it is important to measure T simultaneously with SC for automatic temperature compensation.

1. Connect the SC probe to the meter being used according to the manufacturer's instructions.
2. SC probe should be rinsed with DI water and blotted dry with lab tissue in between each solution, including calibration standards, QA check samples, and samples.
3. Many meters and sondes utilize one-point calibration for SC, although some meters allow for multi-point calibrations. The calibration standard, temperature, and cell constant (one-point calibration) or slope and intercept (multi-point calibration) should be noted on the field sheet. Calibrations may be performed in the laboratory prior to field measurements; if this is the case, then the date of the calibration should also be noted on the field sheet. The lot number and expiration date of the calibration standard and QA check sample should also be recorded on the field sheet.
4. Analyze a QA check sample. The value should be within 10% of the expected value. If it is not, recalibrate according to step 3.
5. Measure the SC of the sample by allowing the reading to stabilize and record in the field sheet. Be particularly careful to rinse and avoid contamination if the sample has a low SC value.
9. Up to 10 samples may be measured before the QA check sample needs to be remeasured, as long as less than 2 hours have passed, and the SC meter and electrode have not been moved to a new location. If either of those conditions are not met, then steps 4 and 5 should be repeated. It is acceptable to measure the QA check sample after every sample if desired.
6. At the end of the sampling day, a last QA check sample should be analyzed according to step 4 and recorded on the last field sheet.
7. Store the electrode according to the manufacturer's instructions.

Temperature (T)

Temperature can be measured using a separate thermistor or thermometer, or more commonly, using the thermistor incorporated into the SC probe or a pH triode. If that is the case, record which probe or electrode's temperature value is being used in the field sheet and use that same source consistently through your field program.

1. Ideally, the thermistor's T readout should be verified in the laboratory with a certified thermometer or other method of verification (for example, ice-water method). Thermistors are generally stable and may only need to be checked as recommended by the manufacturer.
2. If using a separate thermistor or thermometer, the probe should be rinsed with DI water and blotted dry with lab tissue in between each solution measured.
3. Measure the T of the sample when stable and record in the field sheet. If using a flask, observe whether the T rises over the course of pH and SC measurements, and consider refreshing the sample in the flask or setting the flask in the outflow to prevent warming/cooling, use a flow-through cell, or measure field parameters *in situ* to get more accurate measurements.

Oxidation-Reduction Potential (ORP) (OPTIONAL)

Oxidation-reduction potential, also called Eh, measures the potential in a water sample across a platinum electrode, relative to the standard hydrogen electrode. Eh measurements are susceptible to several limitations, including disequilibrium conditions in the water and slow or low electrochemical response to the electrode surface for some redox couples. However, in waters with high iron concentrations, which is often the case for mine-impacted waters, Eh can be a valuable measurement, at least qualitatively.

Eh should be measured in the field, *in situ* or in a flask or beaker filled with sample as close to ambient conditions as possible. If it is not possible to measure Eh in the field, an additional sample split may be collected, stored in a clean bottle, filled to the brim with sample water, and chilled during transport and storage at the lab. Measurements must be made within 48 hours but should not proceed if there are visible precipitates or color changes in the sample split. This deviation in procedure should be noted in the field sheet.

1. Attach the electrode to the meter (if not already in a sonde) and prepare electrode according to manufacturer's instructions (for example, adding filling solution and wetting the junction). Meter output will typically be in mV; if using the same meter for multiple measurements, the output setting may need to be adjusted for ORP. The electrode and filling solution details should be recorded in the field sheet.
2. When measuring Eh, the electrode surface should be suspended in the solution and if using a container, the electrode surface should not touch the bottom.
3. When moving electrode between solutions, the electrode should be rinsed with DI water and blotted dry with a lab tissue to prevent cross contamination.
4. Check electrode performance using Zobell's solution or manufacturer's ORP solution; note that the solution may contain harmful compounds and waste should be disposed of properly. The expected value of the check solution is dependent upon the electrode-filling solution combination and is temperature dependent. It will be useful to bring a table of expected values (in V or mV) of the check solution with the specified electrode/filling solution combination as a function of temperature. These tables are usually available in the electrode manual or from the manufacturer. The value should be ± 10 mV of the expected value and recorded in the field sheet. The check solution only needs to be measured before the first sample of the day, or if the electrode surface show signs of any visible change (scratch, tarnish, etc.) to verify the electrode's performance.
5. Place the electrode in the sample and allow the reading to stabilize and record the Eh of the sample in the field sheet. Eh measurements may take up to 30 minutes to stabilize and should be done at a constant temperature. If the reading does not stabilize in 30 minutes, a note should be made in the field sheet.
6. Clean and store the electrode according to the manufacturer's instructions.

Dissolved Oxygen (DO) (OPTIONAL)

Dissolved oxygen can be measured by a colorimetric method (Rhodazine D or Indogo Carmine) in the field with a commercially available kit. The kits rely on reagent ampules that react with sample water to produce a color. The kits may have a calibration color chart or use a portable spectrophotometer to convert color saturation in the reacted ampule to concentration of DO. It is important that the manufacturer's instructions are followed carefully, particularly regarding collection requirements and wait times for analysis, as inclusion of atmospheric oxygen can compromise the analysis. There are several caveats to be aware of with this technique that may be encountered at mine or mill sites:

- Copper, chromium(VI), and iron(III) can affect the results, causing a significant analytical bias; see the manufacturer's instructions for more details. Although it may not be possible to know in the field whether these elements are present at concentrations that affect the DO results, when the cation results are returned, the DO data may need to be qualified or discarded if they exceed the method limits for DO.
- Low pH waters (about pH 2 or less) can compromise the analysis. DO should not be reported if the pH is low enough to bias the results.

Dissolved oxygen may also be measured by meter and calibrated DO probe, if available. There are several types of probes, each with unique maintenance requirements. A meter and probe setup is more expensive than the colorimetric method and requires calibration by one of several methods. In addition, membrane probes may become clogged by ferric iron precipitates in mine affected waters, producing erroneous results.

Regardless of which method and manufacturer is chosen for DO measurements, the details should be recorded in the field sheets. It is important to measure DO *in situ* or as close to the source water as possible, as DO will ingas/degas over time and as the water temperature changes. Also, relative saturation depends upon temperature and elevation, and it is important that these parameters be noted on the field sheet.

Field notes and observations

Field sheet requirements

Each site and sample unit (if applicable) should be assigned a unique location ID. When sampling each location, a unique field sheet should be assigned for each sampling event. The field sheet may be digital or hard-copy format. If hard-copy, notes must be taken in ink, not pencil. The field sheet must contain:

- Site ID and sample unit (if applicable) = unique location ID
- Description of the sample type (for example, tailing composite sample, pit lake water sample)
- Geospatial data (see below)
- Date and time of sample collection
- Sampling staff names
- Weather conditions at the time of sample collection, and recent weather affecting collection conditions, if applicable
- Other notes/observations.
- Photo of the sample site(s). For composite samples, an overview photo of the site is sufficient.

For water samples, additional information must include:

- Checklist of splits of samples collected for water samples
- Field parameters (pH, T, SC, ORP, DO) and associated calibration, check standard information
- Filtration system used
- Flow measurement technique and source of data

Example field sheets are given for your reference in Appendix 1 (tailings composite samples) and Appendix 2 (water samples).

Additional recommended observations

There are many additional pieces of information that are useful and can be documented in field and/or subsequent lab notes. These are not required but recommended. Additional information could include observations regarding: .

- Munsell field soil color and notes on textures for solid samples
- Depth of piles and method used, if measured in the field
- Description of location, type, and extent of efflorescent salts
- Moisture content of solids
- Vegetation, site cover
- Presence of wetlands or pools of water not sampled
- Erosional features
- Hardpans
- Seeps and description of biofilms, if present
- Paste pH
- Handheld X-ray fluorescence (pXRF)
- Additional photographic documentation

Field sheets should be backed up digitally by scanning hard-copy sheets or a separate backup for digital sheets upon return from the field to prevent data loss. Digital versions of all field sheets will be part of the final data delivery requirement to the USGS.

Geospatial data

Tailings: composite sample sites

Subsample locations can be selected prior to field work using aerial photos, satellite imagery, or other current maps. If any deviations are made from the planned locations, the actual subsample locations should be recorded on-site with a GPS, along with the datum used. If subsample locations are determined in the field, all subsample locations should be recorded on site. Notes as to how subsample locations are determined, and any deviations should be noted in the field sheets. All actual subsample locations should be documented in the final report.

Water: sampling locations

Each water sample site should be recorded on-site with a GPS, along with the datum used.

Site and feature boundaries: polygons

Site boundaries may be determined by the perimeter of all the mine features, land ownership, and/or natural features such as topography. Within a site, there may be one of more mine features, including tailings piles, mine workings, mill workings, pit lakes, adits, waste rock piles, overburden, etc. Please consult with Earth MRI task 8 (Inventory task) for guidance on performing a site inventory and identifying categories of features. For the purpose of this effort, the perimeter of the features to be sampled are important to measure or estimate. If safe to do so, waypoints collected along the perimeter of the feature to be sampled can provide the necessary GIS polygon. Alternatively, current satellite imagery, airborne photography, or other current data can be used to estimate the feature perimeter, as long as the method used is documented in the final report. If multiple features are to be sampled at a site, each feature should have a perimeter defined. For flowing adits, a single GPS point of emergence will suffice for the feature location.

Data for volume estimates

Tailings piles

Approaches for estimating volumes and masses of mine waste piles may vary, particularly with regards to the third dimension. However, please clearly describe the methodology used, including assumptions for estimating volumes of solid piles in the final report.

Flowing adits

The discharge value at the time of sampling should be used to calculate the metal loads and is an important measurement. If the flow is highly seasonal, any data on seasonal flow variation are useful in refining the load calculations. This information and methodology should be discussed in the final report.

Pit lakes

The volume of the pit lake should be estimated or measured. The data may come from a site manager, and/or direct measurement via geophysical or remote sensing data. This information and methodology should be discussed in the final report.

Sample Submission and Geochemical Analyses

Geochemical analyses will be performed at the USGS and/or USGS contract lab(s). All samples will be handled and analyzed using the same sample methods to provide an internally consistent and comparable data set. Solid samples will be ground and homogenized prior to analysis at the USGS laboratories. Please note that water samples for anions and alkalinity/acidity have a 30-day holding time from collection to analysis, so timely shipping of these samples is essential for quality analysis.

Sample Submission

Samples will be submitted to the USGS Sample Control using the following process:

1. Email sample control at MTSampleControl@usgs.gov specifying Earth MRI Mine Waste Characterization to obtain the sample submittal spreadsheet and fill out the spreadsheet. Most fields are completed with drop down boxes. For those without dropdown boxes, such as sample comments, additional information up to 255 characters can be added. Take note of the following when submitting jobs:
    a. Only one sample media per job
    b. Maximum of 45 samples per job
    c. All samples in a job will be analyzed by the same set of analytical protocols
    d. Each sample needs to be assigned a unique field identifier
    e. Project identifier should be included with each job
2. Email the spreadsheet(s) to MTSampleControl@usgs.gov. Also, print a copy of the submittal spreadsheet for each job and include it in the shipment of samples (every box/cooler). If water samples are being shipped, place printed sheet in a sealable bag to prevent water damage.
3. Confirm that the paperwork matches the physical samples, including that the sample names in the spreadsheet match the sample labels. If you find errors, contact sample control.
4. Prevent the spread of invasive species. Make sure that the samples are free of roots, seeds, and insects. Be aware that some samples from certain areas are subject to United States Department of Agriculture (USDA) Federal regulations. Due to penalties for violation of USDA Federal regulations and in accordance with USDA guidelines, failure to follow the required shipping procedures will result in the immediate destruction and disposal of your samples upon receipt by USGS Sample Control.
5. Package your samples for shipping, making sure each sample bag or container is sealed to prevent spillage, leakage, and cross-contamination.
    a. Consider using hard-sided shipping containers rather than cardboard boxes. Fill the voids in the shipping container to prevent sample damage during shipping.
    b. Water samples requiring chilled conditions (anions and alkalinity/acidity) need to be shipped on ice or with cooling packs in a cooler. Place ice in leak-proof bags (or double-bag) because standard bags for ice purchased commercially are not sufficient to prevent melted water from leaking and/or contaminating samples.
    c. Encircle the shipping container in all three dimensions with strips of strapping tape, especially for boxes. Carefully seal the shipping container openings as rough handling of heavy containers often causes sealed edges of containers to split open.
    d. Hard-side containers should not exceed 50 pounds total weight, and boxes should not exceed 35 pounds total weight.
    e. Please include a return label if you would like your coolers or other shipping containers returned to you.
6. Include your return address and ship to:

Sample Control
U.S. Geological Survey
Denver Federal Center, Building 20
Box 25046, MS 973
Denver, CO 80225

Solid phase analyses

Metals and other elemental analyses

Solid samples will be crushed, ground, and homogenized by the USGS prior to submitting samples for analysis. to a contract laboratory for analysis. The methods used by the contract laboratory are briefly described here. Cations and metals will be measured by preparing the sample for analysis using a sodium peroxide fusion method in which samples are fused at 750 °C with sodium peroxide and the fusion cake redissolved in dilute nitric acid. Sixty-one elements are analyzed in the dissolved cake by inductively coupled plasma mass spectrometer (ICP-MS) and ICP optical emission spectrometry (ICP-OES). Elemental analytes are Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, In, K, La, Li, Lu, Mg, Mn, Mo, Nb, Nd, Ni, P, Pb, Pr, Rb, Re, S, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr. Major elements are determined by dissolving the sample into a lithium metaborate/tetraborate fusion disk and measuring major element oxides by wavelength dispersive X-ray fluorescence spectrometry (WDXRF). Analytes are Al_2O_3, BaO, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, SiO_2, TiO_2, SrO, V_2O_5, and Loss on Ignition (LOI). Gold, palladium and platinum are determined by lead fusion fire assay in which the precious metals are separated from the rest of the sample in a flux, and the lead and other base metals removed. The precious metals are dissolved in aqua regia and analyzed by ICP-MS and ICP-OES. Inorganic carbon is determined by treating the sample with perchloric acid and measuring the resulting carbon dioxide with an infrared detector. Total sulfur and total carbon are determined by sample combustion and infrared detection of sulfur dioxide and carbon dioxide gas. Mercury is determined by cold vapor atomic absorption spectrometry (CVAAS). Fluorine is determined by digestion and measurement with a F ion selective electrode.

Mineralogy

Mineralogy will be determined by powder X-ray diffractometry (XRD) using a spiked Rietveld method (Albinati and Willis, 2006) by USGS laboratories.

Acid-base accounting

The method used is based on the method developed by the US Environmental Protection Agency (USEPA; Sobek, et al., 1978)). A sample aliquot is subjected to a preliminary fizz test to determine the volume and concentration of acid to be used. Another aliquot is reacted with water to measure the paste pH. Based on this information, the sample is dosed with acid and back-titrated with base. From this information, the neutralization potential (NP), the acid generating potential (AP), and the net neutralization potential (NNP) can be calculated.

QA/QC

QA/QC practices managed by the USGS include submission of analytical duplicates and standard reference materials as unknowns. Samples will be analyzed with 20% submitted as analytical duplicates. In addition, reference materials similar to the submitted materials will be included as blind samples to the analytical laboratory. The performance of the duplicates and reference material analysis will be evaluated and reported.

Aqueous analyses

Acidified samples will be analyzed by ICP-MS and ICP-OES for Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sn, Sr, Ta, Tb, Te, Th, Tm, Ti, Tl, U, V, Y, Yb, Zn, and Zr. Anions will be analyzed in filtered, unacidified samples by ion chromatography. Alkalinity or acidity titrations will be performed based on the field pH of the sample. The maximum time that samples can be held before analysis (holding time) is 1 year for cations and 30 days for anions and alkalinity/acidity. The data will be qualified when data are released if analyzed after their holding time has passed.

QA/QC

In addition to field blanks and duplicates, the USGS will submit additional reference water samples as blind samples to the laboratory. The performance of the blanks, duplicates, and reference material analysis will be evaluated and reported.

Sample archive

Solid samples will be archived at the USGS in Denver, CO. Bulk materials (prior to crushing and grinding) (300 g – 500 g) as well as ground and prepared materials (30 g – 50 g) will be archived for future analyses. Water samples will not be archived.

Data Reporting

All geochemical data will be reviewed and released to the public through USGS data releases.

Disclaimers

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. This draft manuscript is distributed solely for the purposes of scientific peer review. Its content is deliberative and predecisional, so it must not be disclosed or released by reviewers. Because the manuscript has not yet been approved for publication by the U.S. Geological Survey (USGS), it does not represent any official USGS finding or policy.

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Appendix 1: Example tailings field sheet

Earth MRI Mine Waste Characterization
YY GEOLOGICAL SURVEY

FIELD DATA SHEET Example Tailings Site, County, YY State 20XX

Tailings composite sample

Sample ID____
Site and Sample Unit____
Date____
Time____
Collected by: ____
Photo(s) taken (Y/N) _____

Description of site and sample unit:

____
____
____
____

Description of tailings: surface and subsurface color? Moisture content? Material size and variability?

____
____

Sieving notes:

____
____

Detailed site description and site notes:

Sampling equipment used; other notes: Vegetation? Efflorescent salts? Seeps/drainage/erosional features? Notes on geology/mineralogy? Pile stability? Nearby water bodies?

Weather notes: current conditions? Recent precipitation?

Sample ID____
Date____

Latitude/longitude of subsamples (description of how data collected and/or data collected):

Additional data collected (paste pH, pXRF, etc):

Geospatial data (description of measurements if made in the field):

Samples are labeled with:

- Unique ID number
- Date/time
- Project ID

Appendix 2: Example water sample field sheet

Earth MRI Mine Waste Characterization

YY GEOLOGICAL SURVEY

FIELD DATA SHEET Example Water Site, County, YY State 20XX

Water sample

Sample ID____

Site Name____

Date____

Time____

Collected by: ____

Latitude____

Longitude____

Datum____

Elevation ____

Photo(s) taken (Y/N) _______

Description of site and water body location:

____

____

____

FIELD PARAMETERS

pH ____________________

Calibration: Buffers, lot, exp:

____

____

____

Calibration slope_________

Pass/Fail (92%-102%)?_____

pH QA check_____________

Pass/Fail (+/- 0.05)?_______

ORP (mV)______________

ORP check________________

Pass/Fail (+/- 10mV)?________

DO ________________mg/L

Method__________________

Flow/discharge_________

Method___________________

Temp _______________°C

Source of T_____________

Conductivity________µS/cm

Calibration standard, lot, exp:

____

Cell constant_______________

Temperature_______________

QA check___________µS/cm

Pass/Fail (+/- 10%)?__________

Filter type/filtration setup:

____

____

Water collection method:

____

____

SAMPLES COLLECTED

WATER

___ Metals/Cations - RA

___ Metals/Cations – FA

___ Precious metals- FA

___ Anions - FU

___ Alkalinity/acidity - FU

Other samples collected:

____

____

Sample ID ____

Date____

Detailed site description and site notes:

Water description (color, cloudiness, other); additional site notes (water source, treatment plant, other); electrodes used for field parameters; vegetation? Efflorescent salts? Biofilms? Insects/aquatic life?

Weather notes: current conditions? Recent precipitation?

Discharge/flow measurement (description and/or data collected):

Useful supplementary information for field sheets:

Analysis	Bottle	Preparation	Filtration	Preservation	Label suffix
Metals and cations, raw	125 mL plastic bottle	Acid wash	None	1% v/v concentrated nitric acid	-RA
Metals and cations, filtered	125 mL plastic bottle	Acid wash	Filter (0.45 µm)	1% v/v concentrated nitric acid	-FA
Precious metals	125 mL plastic bottle	Acid wash	Filter (0.45 µm)	1% v/v concentrated nitric acid	-FA
Anions	125 mL plastic bottle	Deionized water rinse	Filter (0.45 µm)	Chill at 4 °C	-FU
Alkalinity/acidity	125 mL plastic bottle	Deionized water rinse	Filter (0.45 µm)	Chill at 4 °C	-FALK

Bottles are labeled with:

- Unique ID number with preservation (label suffix)
- Date/time
- Project ID
- Analysis type