



**Protocol for collection, storage,  
preparation and analysis of  
volcanic ash samples  
for assessment of leachable  
elements**



## Table of Contents

1. INTRODUCTION .....	3
2. LIST OF ABBREVIATIONS .....	3
3. ASH COLLECTION .....	4
4. SAMPLE STORAGE AND PREPARATION .....	5
5. QUALITY ASSURANCE AND CONTROL MEASURES.....	5
6. DEIONIZED WATER LEACH.....	6
6.1 Overview of method.....	6
6.2 Equipment required .....	6
6.3 Reagents required .....	6
6.4 Leaching procedure .....	6
6.5 Re-extractions.....	7
6.6 Instrumental analysis.....	7
7. SIMPLE GASTRIC LEACH.....	8
7.1 Overview of method.....	8
7.2 Equipment required .....	8
7.3 Reagents required .....	9
7.4 Reagent preparation.....	9
7.5 Leaching procedure .....	9
7.6 Instrumental analysis.....	9
8. DATA REPORTING .....	10
9. QUICK REFERENCE FLOW CHART .....	11

## 1. INTRODUCTION

Freshly-erupted volcanic ash contains a range of readily soluble elements, which may be released either rapidly or more slowly upon contact with water or body fluids. This can cause both beneficial effects (such as the addition of plant growth nutrients to pastoral systems) and harmful effects (such as fluorine toxicity to livestock). Therefore, there is a need for standard and reliable methods for hazard assessment of readily soluble elements following volcanic ashfall, to provide timely and reliable information to emergency managers.

This document is a practical users' guide to the implementation of two leaching methods developed specifically for analysis of volcanic ash: a deionized water leach and a simple gastric leach. Guidelines for ash collection and preparation are also included.

The **deionized water leach** assesses the dissolution of readily water-soluble compounds on ash particle surfaces. It is applicable to situations such as predicting compositional changes in roof catchment rainwater tanks and open livestock water troughs, runoff into surface waters and availability of plant growth nutrients for immediate uptake by crops. It is the most frequently used method and, therefore, appropriate for comparability with other data sets. It can also be used to assess inhalation hazards of volcanic ash in the absence of a simulated lung fluid leach in this protocol.

The **simple gastric leach** is intended to estimate the bioaccessible fraction of toxicants such as fluoride, arsenic and lead that are solubilised from ash surfaces if ash is ingested by humans or livestock. It is adapted from more complex methods for estimating bioaccessibility.

These methods are designed for users without specialised training, using commonly available laboratory equipment.

## 2. LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
HDPE	High density polyethylene
IC	Ion chromatography
ICP-MS	Inductively-coupled plasma mass spectrometry
ICP-OES	Inductively-coupled plasma optical emission spectrometry
ISE	Ion selective electrode
IVHHN	International Volcanic Health Hazard Network

### 3. ASH COLLECTION

- For hazard assessment, it is generally most appropriate to collect samples from population centres and/or agricultural areas, depending on purpose.
- Ensure that sampling captures the spatial and temporal variability of the whole deposit as far as possible, within the areas of interest.
- **For any quantitative analysis of leachate compositions, the collection of pristine (dry, not rained on) samples is of absolute importance.** However, sometimes ash will fall 'wet' and will still yield useful information. Always record the state of the sample, particularly whether or not it has been affected by rainfall prior to collection.
- If the ash deposit appears heterogeneous, we recommend collecting multiple samples at each site to allow sampling variability to be determined. Alternatively, multiple samples may be composited and homogenised into a bulk sample for that site, thus reducing sampling variability.
- Ideally, collect ash in pre-deployed clean plastic trays. To calculate ash loading (in kg/m<sup>2</sup>), record the area of the tray and the total weight of the ash collected.
- If trays cannot be pre-deployed, collect samples from hard, flat, clean, and dry surfaces such as concrete steps or outdoor tables. Avoid locations where surface dust or other debris have accumulated. **Always record the surface each sample is collected from.** If possible, leave a small margin between the bottom of the sample and the surface to minimise the chance of contamination from the surface. This may not be possible for thin deposits.
- If possible, collect at least 50 g of ash per sample. While leachate analyses may be performed on a few g of ash or less, larger samples allow for more options such as replication and supporting analyses.
- Collect samples into self-sealing plastic bags or airtight plastic containers. Ensure that each ash sample has a unique sample number.
- At each site, record the following information:
  - site coordinates/location
  - date and time of sample collection
  - If a plastic tray was used, record the area of the tray, the weight of the sample and the thickness of the deposit
  - If sample was collected from an existing surface, record the thickness of the deposit and the surface collected from (*e.g.*, concrete, treated timber, galvanised iron roof)
  - Time since ashfall, if known
  - Whether ash fell wet or dry, if known
  - Whether deposit has been affected by rainfall, if known.

For further comprehensive advice on ash collection methods see:

- USGS Alaska Volcano Observatory website <https://avo.alaska.edu/ashfall.php> [this site describes procedures for collecting measured-area samples in detail].
- IVHHN website [http://www.ivhhn.org/uploads/en/IVHHN\\_Ash\\_Collection\\_Procedures.pdf](http://www.ivhhn.org/uploads/en/IVHHN_Ash_Collection_Procedures.pdf) [this site describes general ash collection methods in detail].

Be aware that some general ash collection methods are unsuitable for leachate analysis, such as devices that collect both ashfall and rainwater.

#### **4. SAMPLE STORAGE AND PREPARATION**

- Weigh all samples in field state upon arrival at laboratory.
- Dry samples before analysis or long-term storage. Samples should be dried at room temperature in an open sample bag or plastic tray. To minimise loss of volatiles, do not dry in an oven. Dry for at least 12 hours to constant weight and record final weight.
- If necessary, sieve bulk samples through 2 mm mesh to remove large debris.
- Homogenise each sample by gently rotating the sample container.
- If sample splits are required for different analyses, use the 'cone and quarter' method using a plastic knife. Alternatively, use a spinning riffler or Jones splitter.
- If possible, store samples in a desiccator to prevent absorption of moisture from the atmosphere.
- Report if any condensation is observed in the container during or after storage.
- Avoid long periods of storage before analysis to reduce the potential for ongoing surface reactions.

#### **5. QUALITY ASSURANCE AND CONTROL MEASURES**

- Always run a procedural blank with each batch of samples. A procedural blank is a solution of the extractant only that is subjected to all processing steps to monitor contamination acquired during all stages of the procedure. Inclusion of multiple procedural blanks allows variability in blank quality to be evaluated. Leachate concentrations should be corrected for any blank contributions.
- Ensure adequate replication to assess analytical variability. Include at least one duplicate per batch of ten samples.
- The quality of analytical data can be checked by calculating the electrical balance between cations and anions. This may be done manually, or using the open access geochemistry program PHREEQC (<https://www.usgs.gov/software/phreeqc-version-3>).

## 6. DEIONIZED WATER LEACH

### 6.1 Overview of method

The deionized water leach reflects the dissolution of readily water-soluble compounds adsorbed onto ash particle surfaces.

Subsamples of ash are leached with deionized water at ratios of 1:20 and 1:100 g ash:mL water, for one hour. Following centrifugation or settling, the supernatant is filtered for determination of cations and anions.

### 6.2 Equipment required

- Analytical balance accurate to 0.01 g or better
- Plastic spatula for weighing out samples
- Extraction vessels (preferably polycarbonate, polypropylene or polyethylene centrifuge tubes, but glass beakers or flasks will suffice)
- Pipette or autopipette
- Shaker (orbital or horizontal table shaker, rotating or end-over-end shaker). The use of a rotating or end-over-end shaker is preferable to promote thorough mixing.
- Centrifuge (optional but recommended)
- Filtration apparatus (either vacuum filtration unit or syringes and syringe filters)
- 0.45  $\mu\text{m}$  and 0.2  $\mu\text{m}$  filter paper or syringe filters (nylon, glass fibre or nitrocellulose)
- Filtrate collection vessels (preferably HDPE tubes or bottles)
- pH meter
- Conductivity meter
- Deionized water wash bottle
- Plastic beakers for measurement of pH and conductivity

### 6.3 Reagents required

- Deionized water, preferably 18.2 M $\Omega$  resistivity at 25°C.
- Analytical grade HNO<sub>3</sub> (nitric acid), for cleaning of equipment.

### 6.4 Leaching procedure

- For each sample, carry out extractions at ratios of both 1:20 and 1:100 g ash:mL water.
- Weigh out a subsample (preferably at least 1 g) from the homogenised bulk ash sample into a centrifuge tube (or alternative vessel such as beaker or flask). Record the weight to the nearest 0.01 g.
- Add deionized water to the tube or flask to the desired ratio (*e.g.*, for 1:20 ratio, add 20 mL deionized water to a 1 g subsample). Weigh the tube before and after adding water to check

the accuracy of the volume added. An approximate minimum volume of 20 mL should be sufficient for all analyses, although be aware that some instrumental methods such as flame AAS require larger volumes.

- Shake the tube or flask gently by hand for 10 seconds.
- Agitate the sample for one hour using a shaker. Ensure thorough mixing between the ash and the leaching solution. If no mechanical shaker is available, shake samples frequently by hand, ensuring contact time of one hour.
- Centrifuge samples at 3000-5000 rpm for 5-10 minutes. Samples with high proportions of very fine ash may require longer.
- If a centrifuge is not available, allow samples to settle for 10 minutes.
- Take an unfiltered aliquot of leachate for determination of pH and conductivity.
- Filter samples through 0.45  $\mu\text{m}$  filters. Note that filtration through 0.2  $\mu\text{m}$  filters may be required if anions are analysed using IC with a low capacity ion exchange column.
- Collect separate aliquots for cation and anion analysis.
- Collect filtrate in HDPE bottles. Pre-rinse bottles with a small amount of filtrate.
- Preserve aliquot for cation analysis in 1% v/v analytical grade nitric acid.

## 6.5 Re-extractions

Re-extractions are advised in situations where fluoride may be present as slowly soluble compounds or where very high concentrations of elements such as sulphur may lead to saturation of the leachate solution.

### Re-extraction procedure:

- During first extraction, ensure that as much solid as possible is retained in extraction vessel when supernatant is decanted and filtered. Record weight of tube plus residual ash and extractant. Add deionized water to the desired ratio (1:20 or 1:100) and re-weigh tube. Continue with extraction as per leaching procedure (Section 6.4).
- If applicable, reserve the filter paper when supernatant from first extraction is filtered; dry and weigh to determine the mass of ash lost from the original mass.
- Repeat the previous two steps for any further re-extractions.

## 6.6 Instrumental analysis

- Cations may be determined by the following methods:
  - AAS
    - Flame AAS is suitable for major cations such as Ca, Mg and Na
    - Graphite furnace AAS is suitable for trace elements such as Cu and Zn
    - Hydride generation AAS is suitable for As
  - ICP-OES
  - ICP-MS

- Anions may be determined by the following methods:
  - IC
  - ISE for fluoride and chloride ion
  - Ferric thiocyanate colorimetry for chloride ion
  - Turbidimetry for sulphate ion

## **7. SIMPLE GASTRIC LEACH**

### **7.1 Overview of method**

The simple gastric leach is intended to estimate the bioaccessible fraction of toxicants such as fluoride, arsenic and lead that are solubilised from ash surfaces if ash is ingested by humans or livestock. It is adapted from more complex methods for estimating bioaccessibility.

Subsamples of ash are leached with 0.032 M hydrochloric acid (HCl) at a ratio of 1:100 g ash:mL leachant, for one hour. Following centrifugation, the supernatant is filtered for determination of potential toxicants of interest.

For assessing ingestion hazards to livestock, using the bulk ash sample is appropriate, but for assessing ingestion hazards to humans the size fraction <250 µm is preferable because the most important ingestion pathway for children is thought to be hand to mouth transfer of finer size fractions which have adhered to the hands. Elements of interest typically include fluoride and trace elements such as arsenic, cadmium, copper, iron, lead, nickel and zinc.

### **7.2 Equipment required**

- 250 µm sieve with plastic mesh
- Analytical balance accurate to 0.01 g or better
- Plastic spatula for weighing out samples
- Extraction vessels (preferably polycarbonate, polypropylene or polyethylene centrifuge tubes, but glass beakers or flasks will suffice)
- Pipette or autopipette
- Shaker (orbital or horizontal table shaker, rotating shaker or end-over-end shaker). The use of a rotating or end-over-end shaker is preferable to promote thorough mixing.
- Centrifuge (optional but recommended)
- Filtration apparatus (either vacuum filtration unit or syringes and syringe filters)
- 0.45 µm and 0.2 µm filter paper or syringe filters (nylon, glass fibre or nitrocellulose)
- Filtrate collection vessels (preferably HDPE tubes or bottles)
- pH meter
- Deionized water wash bottle



### 7.3 Reagents required

- Deionized water, preferably 18.2 MΩ resistivity at 25°C.
- Analytical grade HNO<sub>3</sub> (nitric acid), for cleaning of equipment.
- Analytical grade HCl (hydrochloric acid).

### 7.4 Reagent preparation

To prepare the simple gastric leaching solution, use 2.58 mL 12.4 M (38%) analytical grade HCl per one litre of deionized water. Always add the acid to the water. Measure pH and adjust to pH 1.5 with deionized water or additional HCl if necessary.

### 7.5 Leaching procedure

**To assess hazard to livestock from ash ingestion, use bulk ash sample.**

**To assess hazard to human health from ash ingestion, use the <250 μm size fraction.**

- Weigh out a subsample (preferably at least 1 g) from an ash sample into an extraction vessel. Record weight to nearest 0.01 g.
- Add 0.032 M HCl to tube or flask to a ratio of 1:100 g ash:mL leachant. Weigh tube before and after adding water to check the accuracy of the volume added.
- Shake extraction vessel gently by hand for 10 seconds.
- Agitate sample for one hour on a shaker. Ensure complete contact between ash and leaching solution. If no mechanical shaker is available, shake samples frequently by hand, ensuring contact time of one hour.
- Centrifuge samples at 3000-5000 rpm for 5-10 minutes. Samples with high proportions of very fine ash may require longer.
- If a centrifuge is not available, allow samples to settle for 10 minutes.
- Filter samples through 0.45 μm filters. Note that filtration through 0.2 μm filters may be required if fluoride is to be analysed using ion chromatography with a low capacity ion exchange column.
- Collect filtrate in HDPE bottles. Pre-rinse bottles with small amount of filtrate.

### 7.6 Instrumental analysis

- Fluoride may be determined by IC or ISE.
- Trace elements may be determined by the following methods:
  - AAS
  - ICP-OES
  - ICP-MS

## 8. DATA REPORTING

- Report results in units of mg/kg (dry weight ash).
- Use the following formulae to convert from units of mg/L or µg/L (from analysis of extracts) to mg/kg:

$$\text{mg/kg} = \text{mg/L} \times \text{L/kg}$$

$$\text{mg/kg} = 0.001 \times \mu\text{g/L} \times \text{L/kg}$$

**Where:**

**mg/L** is the concentration of the element in the extract, adjusted for any contribution from the procedural blank and accounting for dilution factors.

**L/kg** is equivalent to mL/g and is the ratio of leachant to ash (*e.g.*, 0.99 g ash to 20.00 mL deionized water gives a ratio of 20.2).

## 9. QUICK REFERENCE FLOW CHART

