

SAMPLE PREPARATION FOR Cl-36 ANALYSIS BY AMS

Summary

This method is used to extract and purify Cl from silicate or carbonate rock samples and produce AgCl for AMS analysis. After dissolution, Cl is separated from the rock matrix by AgCl precipitation. This precipitate is re-dissolved in NH_3 and Cl separated from S (including ^{36}S , an interfering isobar of ^{36}Cl) by BaSO_4 precipitation. AgCl is recovered by acidifying the $\text{Ag}(\text{NH}_3)_2^+:\text{Cl}^-$ solution, then recovered and dried for AMS analysis. The procedure can be used with or without added Cl^- carrier. Adding isotopically-normal Cl^- carrier decreases propagation of $[\text{Cl}^-]$ measurement errors into the calculation of ^{36}Cl exposure ages and guarantees recovery of a measurable amount of AgCl. This is standard procedure at UW. We do not currently use the method with an isotopically-enriched carrier (^{35}Cl or ^{37}Cl), but it could easily be adapted for that purpose (see the accompanying isotope dilution method for $[\text{Cl}^-]$ analysis). When applied to carbonate samples, the method allows Cl^- concentration to be measured on the same solution used for ^{36}Cl analysis. The description includes a sub-sampling procedure tailored to the isotope dilution chloride analysis method used at UW, but the procedure could easily be modified to suit other methods of chloride analysis. When dealing with silicate samples, we analyse for chloride concentration on separate sub-samples of rock rather than splitting the solution from which the AMS sample is prepared. Dissolution of silicates results in so much fluoride precipitation that the resulting solutions cannot be reliably split for Cl^- concentration measurements. We have tested and confirmed on samples of calcite, K-feldspar and whole-rock dolerite, that sample Cl^- , carrier Cl^- and sample $^{36}\text{Cl}^-$, which likely enter solution at different stages of the procedure, equilibrate isotopically before the first AgCl precipitation. In addition to these rock types, we have used the method successfully with samples of dolomite, Ca-feldspar, and whole-rock basalt, andesite and rhyolite. Best results are almost always obtained on separated Ca- and K-rich minerals, which yield higher $^{36}\text{Cl}/\text{Cl}$ ratios than their parent rocks. The method is designed to be used on samples of < 20 g (~ 10 g of calcite or K-feldspar is typical). We have not tested it on larger samples, which would produce unmanageably large dissolution volumes, making it difficult to precipitate and collect AgCl. Yields vary with sample size and the amount of Cl^- , suggesting that most losses occur due to incomplete precipitation and recovery of AgCl. With practice, yields of 75-80% can be obtained on samples containing ~ 1.25 mg of total Cl^- (carrier plus native Cl^-). Better yields are usually obtained on samples containing more Cl^- , and *vice versa*. It is difficult to recover sufficient AgCl for AMS measurements from samples containing less than 1 mg total Cl^- .

Version

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References

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Stone J.O., Fifield L.K., Allan G.L. and Cresswell R.G. (1996) Cosmogenic chlorine-36 from calcium spallation. *Geochimica et Cosmochimica Acta* 60, 679-692.

if you use this method.

(1) Sample pre-treatment

For surface samples, saw to a slab of measured thickness (3-5 cm).

Remove any adhering soil, lichen etc. Grind off weathered or rusty surfaces, noting the thickness of rock removed.

Saw or split into 1-2 cm chips.

If sample has been put through the jaw crushers, sieve and retain chips > 1 cm only. Rinse in water until no further fines wash off and dry overnight.

Crush coarsely in TEMA mill. Sieve (brass or preferably nylon mesh) and collect the 125 - 250mm or 250 - 500mm fraction for the AMS preparation (the size fraction should be finer than the rock's grain size, to ensure that grain boundaries are exposed to leaching). For ^{36}Cl work on mineral separates, the <125mm fraction will also be needed for whole-rock XRF, B, Gd analyses. Keep all other grain size fractions (> 125mm) produced at this stage in case they're needed for mineral separation in future.

Rinse and/or sonicate the AMS fraction until no further fines can be washed out of it. Finish with several rinses in lab de-ionised water. Dry overnight.

(2) Leaching

For carbonates...

Tare and label a clean 400 mL pyrex beaker. Add 20 - 25g dry sample. Add ~ 100 mL of MQ water and swirl to wet the sample thoroughly.

In a separate beaker, mix 15 mL 2M HNO_3 (i.e. enough to dissolve 1.5g of CaCO_3) and 50 - 100 mL of MQ.

Pour into the rock sample beaker, and swirl gently to wet the grains. Mix the acid in slowly to prevent foaming. The aim is to get a slow, even dissolution of all the grain surfaces and minimise preferential attack on the finer grains.

Once the reaction has died down a bit, cover the beaker with parafilm (leaving part of the rim unsealed for CO_2 to escape) and stand for 12 - 24 hrs. Swirl gently occasionally.

For silicates...

Tare and label a clean pyrex beaker. Add approx. 20 - 25g dry sample.

For whole rocks, add 100 - 150 mL 2% HNO_3 . For robust separated minerals such as feldspar or pyroxene, use 10% HNO_3 .

Put a glass or teflon stirring rod in the beaker to stop "bumping" and boil gently on the hotplate. Heat to just below boiling for 4-6 hrs, swirling occasionally. Beware of boiling or superheating the liquid in the pile of grains on the floor of the beaker, which can "flash" over and cause the beaker to jump about on the hotplate. Samples have been lost with beakers that "walked" off the hotplate.

Cool and weigh the beaker.



Rinse 3 - 4 times with MQ and repeat the leaching procedure.

Rinse thoroughly (at least 5x) in MQ water, swirling sample to ensure complete removal of $\text{Ca}(\text{NO}_3)_2$.

Dry overnight in the oven at 70° . The sample weight should have decreased by ~ 3 g.

(3) Sample loading

For carbonates...

Label a clean 500 mL serum bottle and tare it (to $\pm 0.1\text{g}$).

Tare a folded ~8 cm square of weighing paper (remove static if necessary!).

Transfer sample grains with a spatula onto the weighing paper (do not pour directly from beaker - this will scatter sample grains into the balance). Limit samples to less than 20 g.

Weigh the sample and record the weight.

Carefully transfer sample to bottle. Transfer should be complete - if any material is lost from the paper, re-weigh the remainder and try again. If any adheres to the paper, re-weigh it after transfer and adjust the sample weight.

Wash in any grains clinging to the neck of the bottle with 5 - 10 mL MQ water.

Slurry the sample to wet it completely.

Decant 20 - 30 mL into a clean centrifuge tube for [Cl] determination. Label the tube. Weigh the remainder.

If the leachate is to be analysed for ^{36}Cl , decant the remaining solution into a clean beaker. Weigh the remainder. Precipitate SO_4^{2-} from the solution and collect Cl as AgCl (see below).

Repeat this procedure for a second leaching if required. Rinse thoroughly (at least 5x) in MQ water, swirling sample to ensure complete removal of HNO_3 .

Dry overnight in the oven at 70° .

For silicates...

Label a clean 500 mL FEP teflon bottle.

Tare a folded ~8 cm square of weighing paper (remove static if necessary!).

Transfer sample grains with a spatula onto the weighing paper (do not pour directly from beaker - this will scatter grains into the balance). Limit samples to less than 20 g.

Weigh and record the result.

Carefully transfer sample to bottle. Beware static around the neck of the bottle. Transfer must be complete - if any material is lost from the paper, re-weigh the remainder and try again. If any adheres to the paper, re-weigh it after transfer and adjust the sample weight.

Wash in any grains clinging to the neck of the bottle with 5 - 10 mL MQ water.

Slurry the sample to wet it completely.



(4) Dissolution

For carbonates...

In the fume hood, gradually add 10 mL 2M HNO₃ per gram of sample carbonate to the bottle. To avoid foaming, the acid should be added in aliquots of ~10 mL each 20 - 30 minutes, and the bottle should not be shaken or swirled until dissolution is almost complete. The sample bottle should be kept loosely capped between additions of acid.

Once dissolution is complete, swirl to homogenise the solution, then allow the insoluble fraction to settle.

Weigh the bottle, trying not to re-loft the sediment.

For silicates...

First add the carrier

Remove static from the carrier bottle and weigh it carefully.

Invert the carrier bottle 3-4 times to mix in droplets condensed on the lid and walls. Do not leave droplets clinging to the lid where they will dry out while the bottle is open.

Using a clean pipette tip, transfer carrier containing ~1 - 1.25 mg of chloride into the sample bottle (for the current WIH solution this is ~ 0.2 mL). The carrier solution must be ejected thoroughly from the pipette - if necessary, remove the final droplet by touching the pipette tip to the inside wall of the bottle, then discard the tip. Re-cap the carrier bottle immediately.

Use a few mL of MQ water to rinse in any droplets of carrier clinging to the sample bottle's wall.

Remove static and re-weigh the carrier bottle. Calculate the carrier added. Re-mix the carrier prior to removal of each aliquot. Return the carrier bottle to its plastic bag at the end of each use.

Swirl the sample bottle to mix in the carrier.

Now dissolve the sample

In the fume hood, add sequentially 6 mL 2M HNO₃ and 3.5 mL conc. HF for each gram of sample to the bottle. Recap firmly, but do not seal.

Swirl once and then allow sample to sit quietly. The bottle will heat up, and if swirled vigorously may boil, causing Cl₂ loss and releasing toxic NO₂ + N₂O₄ fumes.



Once the bottle begins to cool down, swirl it gently to break up the fluoride cake (CaF_2 , plus NaMgAl fluoride hydrate and NaCaAl fluorosilicates) and expose remaining sample to the acid.

Place it in a water bath at $\sim 70\text{-}80^\circ\text{C}$ for as long as required to dissolve the sample fully (usually 48hrs or more). Initially it should be swirled \sim hourly to keep the fluorides from caking together and coating undissolved sample grains.

Once dissolution is complete, swirl to mix the solution and allow the fluorides to settle.

For carbonates only

(5) Splitting for chloride analysis, and carrier addition

Tare and label a clean 50 mL centrifuge tube and record its weight. This will eventually be used to collect the insoluble residue from the dissolution.

Tare and label a cleaned 15 mL centrifuge tubes to receive an aliquot for chloride concentration measurement by isotope dilution.

Label a 15 mL polypropylene centrifuge tube to receive a split for Ca-Mg-K-Mn-Fe analysis by ICP.

Transfer 12 - 15 mL of the parent solution (less if you know in advance that the sample has a high Cl content; if possible, aim to remove 80 mg of sample Cl for the isotope dilution analysis, but do not exceed 15 mL) to the 50 mL tube.

Weigh the tube and calculate the weight of liquid removed from the parent solution (this is required to calculate the effective weight of rock sample to which carrier is added for the AMS measurement).

If the solution is still cloudy after standing, centrifuge the tube to obtain a clear supernatant. Otherwise proceed ...

Transfer all but ~ 1 mL of the clear sub-sample to the 15 mL tube for isotope dilution. Leave ~ 1 mL in the large tube.

Weigh the tube containing the isotope dilution sub-sample. Record the weight and calculate the aliquot weight for the chloride analysis.



Dilute the 1 mL remainder in the large tube to 40 mL with MQ water.

Transfer approximately 1 mL of the diluted solution to the small ICP sample tube for Ca-Mg-K-Mn-Fe measurement. When diluted to 10 mL, this will have a Ca concentration of 50 - 100 ppm.

Discard the solution, but not the sediment, from the 50 mL centrifuge tube. Retain the tube for the next step of the procedure.

Now spike the solution

Remove static from the carrier bottle and weigh it carefully.

Invert the carrier bottle 3-4 times to mix in droplets condensed on the lid and walls. Do not leave droplets clinging to the lid where they will dry out while the bottle is open.

Using a clean pipette tip, transfer carrier containing ~1mg of chloride into the sample bottle (for the current WIH solution this is ~ 0.2 mL). Re-cap the carrier bottle immediately. The carrier solution must be ejected thoroughly from the pipette - remove the final droplet by touching the pipette tip to the inside wall of the bottle, then discard it. Rinse down with a few mL MQ water any carrier on the sample bottle wall.

Remove static and re-weigh the carrier bottle. Calculate the carrier added.

Re-mix the carrier prior to removal of each aliquot.

Return the carrier bottle to its plastic bag at the end of each use.

Swirl the sample bottle thoroughly to mix in the carrier and allow it to equilibrate (at least overnight).

(6) Separation from dissolution residue

For carbonates...

Once any sediment has settled again, decant as much of the supernatant as possible into a clean 250 mL pyrex beaker.

Label the beaker, cover it with parafilm and stand it in the fume hood.

Centrifuge the remaining solution in 50 mL batches in the tared centrifuge tube prepared earlier, collecting the insoluble fraction and transferring the supernatant to the beaker as you go.

For silicates...

Label a clean 250 mL PFA teflon beaker (use masking tape).

Decant off as much of the supernatant as possible, without disturbing the fluoride gel, into the teflon beaker. TAKE CARE - THIS IS A STRONG HF SOLUTION.

Cover the beaker with parafilm and stand it in the fume hood.



Complete the transfer of the supernatant by rinsing out the sample bottle with ~10 mL of MQ water.

Complete collection of the sediment with as many further rinses as required. Resuspend the sediment in MQ water, centrifuge it and discard the supernatant. Repeat several times to remove all traces of excess HNO₃. Dry at ~60°C overnight.

Cool for 1hr with the lid slightly open, then weigh the tube. Subtract the residue weight from the sample weight to determine the actual weight of sample dissolved and the weight of the parent solution that was split for AMS and isotope dilution analyses.

Store the residue in case XRF or XRD measurements are required, or quartz is to be separated for ²⁶Al-¹⁰Be analysis.

(7) AgCl + Ag₂SO₄ precipitation

Remove the parafilm from the beaker and heat at setting 3 (teflon) or 3.5 (pyrex) on the hotplate. Take care with the teflon beakers - in the 30-60 min it takes to heat the solution, their bases may soften, but should not be allowed to melt.

Once the solution is convecting rapidly (bubbles will have formed on the floor of a teflon beaker), turn down the lights and add ~1 mL of 10% AgNO₃. The solution should go cloudy within a few seconds. Not having the solution hot enough when the AgNO₃ is added seems to result in fine-grained, powdery AgCl, which is difficult to collect compared to the ideal dense, gummy and flocculent precipitate. This cannot be rectified by heating the solution after precipitation, so make sure the beaker is hot enough beforehand.

Leave the beaker on the hotplate for ~1hr for the AgCl to flocculate. Do not swirl or tilt it - this tends to float the AgCl up onto the meniscus making it difficult to recover.

After an hour, the floor of the beaker should be coated with AgCl and the supernatant fairly clear. A light tap on the base of a glass beaker should gather specks of AgCl at this stage. Small flecks of AgCl will be visible clinging to the bubbles on the floor of a teflon beaker. (Try not to dislodge the bubbles, as this will carry the AgCl to the surface). Take the beaker off the hotplate and allow it to cool. Cover it with parafilm and stand it overnight in the dark to finish clearing (place it in the spill tray in the vented acid storage cupboard beneath the hood).

Using a clean 50 mL centrifuge tube, centrifuge the remaining solution in 50 mL batches, transferring the supernatant to the teflon beaker as you go and retaining any fluoride residue that collects in the tube.

Complete the transfer of supernatant from the sample bottle with a ~10 mL MQ water rinse.

Now add 10 - 20 mL MQ water to the fluoride collected in the centrifuge tube. Shake to resuspend the fluoride and extract any Cl⁻ trapped in the gel (take care in case droplets of the HF solution leak out beneath the lid).

Centrifuge and add the supernatant to the teflon beaker. The fluoride residue should be collected for disposal as hazardous waste.



Tilt the beaker and tap its base to collect the precipitate into a lump in the bottom “corner” (most of the bubbles in a teflon beaker should have re-dissolved into the acid overnight, so there shouldn't be a problem with AgCl floating up onto the meniscus).

Decant off as much solution as possible without losing the AgCl. WHEN WORKING WITH SILICATE SAMPLES - THIS IS A STRONG HF SOLUTION, WHICH MUST BE HANDLED WITH APPROPRIATE PRECAUTIONS AND COLLECTED FOR HAZARDOUS WASTE DISPOSAL. It is usually not worth trying to recover the small amount floating on the surface of the liquid. The contents of one of the 250 mL pyrex or FEP beakers can be reduced to ~35 mL before precipitate stirred up off the floor reaches the pouring spout.

Label a clean conical 50 mL polypropylene centrifuge tube.

Transfer the remaining liquid to the tube. With the teflon beakers, the meniscus will sweep the clumps of AgCl out of the beaker in the last few droplets of solution. With the pyrex beakers, it helps to rock the solution back and forth a bit as it is being poured, to keep the AgCl from grounding and clinging to the glass.

Wash the walls and floor of the beaker with 5 - 10 mL MQ and swirl to collect any remaining flecks of AgCl. Add to the centrifuge tube. Repeat if necessary. Be careful not to splash the sample solution, or flecks of AgCl, from the beaker back onto the spout of the wash bottle.

Tap the tube to concentrate the precipitate into its base. Centrifuge at 2500 RPM for ~ 3 minutes. If the tube is full, do not exceed this speed - the base can deform and split under the stress.

Decant off the supernatant - the clump of AgCl will stick in the point of the tube.

Rinse with 5 - 10 mL MQ, suspend the AgCl, gather it again in the point of the tube and centrifuge at 3000 RPM.

Repeat to collect the final, washed AgCl (+Ag₂SO₄) precipitate. Cap the tube. If pausing at this stage, keep the precipitate in the dark and do not allow it to dry out. (Much better to pause during the next step, however).

(8) Sulfate clean-up

Dissolve the precipitate in 2 mL of 1:1 NH₃ solution (make up with roughly 1 part 28% NH₄OH to 1 part MQ water). Dilute with a further 10 - 15 mL of MQ.

Transfer to a glass centrifuge tube. Rinse out the polypropylene tube (5 - 10 mL of MQ) and add the rinse to the glass tube.

Add 1 mL of saturated BaNO₃ solution to the glass tube. Swirl it gently to mix with the NH₃ solution.



Top up the tube with MQ, cover with parafilm and stand for at least 48 hrs to precipitate BaSO_4 . It can stand for a week if need be - it seems that the longer it stands, the more efficient the sulfur clean-up. In addition to BaSO_4 (fine-grained, granular, translucent to white), several other insoluble compounds may appear in the tube. A trace of extremely fine yellow-brown material may precipitate and settle out gradually (possibly $\text{Fe}(\text{OH})_3$ from Fe carried over with the AgCl). A clumpy pinkish-brown precipitate which darkens if exposed to light is probably Ag_2CO_3 precipitating as the solution absorbs CO_2 from the atmosphere. If Ag_2CO_3 does appear, it will be accompanied by clumps of feathery white BaCO_3 .

Tap the precipitate gently into the base of the tube. Much of it, especially needles of BaCO_3 , will cling to the walls. Don't worry - nothing will budge this material.

Centrifuge the tube for 5 - 10 minutes at 2200 RPM.

Using a clean pipette, withdraw liquid from beneath the meniscus and transfer it to a clean, labelled polypropylene centrifuge tube. Grains of BaSO_4 adhering to the walls of the tube may get dislodged as the meniscus descends. These tend to float onto the liquid surface and can be kept out of the final sample solution by withdrawing it from below the meniscus. Take care not to disturb the BaSO_4 precipitate in the base of the tube - if disturbed, the tube will have to be centrifuged again. Stop the transfer with 2-3 mL of liquid left in the tube, to avoid disturbing the precipitate. The recovered solution should contain ~90 - 95% of the sample chloride - sacrificing 2-3 mL of the supernatant is preferable to carrying over BaSO_4 into the final AgCl precipitate.

(9) Final AgCl precipitation

To recover AgCl from the ammonia solution, label a small (100 mL) pyrex beaker and add to it:

- (i) ~15 mL 2M HNO_3 (AgCl will precipitate from ammonia on acidification - neutralisation of 1 mL concentrated ammonia requires approximately 8 mL 2M HNO_3).
- (ii) ~1 mL 10% AgNO_3 to increase the Ag^+ content of the solution (and make up for Ag^+ lost as Ag_2CO_3).
- (iii) MQ water to ~40 mL.

Heat on the hotplate to just below boiling (setting 3 - 3.5). The solution should be actively convecting - by the time it is hot enough, the volume will have dropped to ~35 mL.

Remove the beaker from the hotplate and add the AgCl solution. The beaker will steam briefly and go cloudy. Rinse out the centrifuge tube with 5 mL of MQ water, and add it to the beaker. Return the beaker to the hotplate for ~1hr. Put the centrifuge tube aside for collection of the final AgCl.

During the heating stage, the solution should decrease in volume to <50 mL (if it looks like falling below ~30 mL, add MQ water and turn down the hotplate slightly). A film of white AgCl flecks should form on the floor of the beaker and the supernatant should gradually clear. Re-suspending the AgCl flecks as they form and circulating them through the solution helps clearing, but beware of



floating AgCl onto the meniscus.

Take the beaker off the hotplate and cool for ~30 minutes. Cover with parafilm and stand in the dark for a further ~ 2 - 4 hrs for AgCl to settle out.

Tilt the beaker and tap its base. The film of AgCl on its floor should clump into large sticky flecks and gather in the bottom “corner” of the beaker.

Discard as much of the supernatant as possible without disturbing the precipitate. Now rock the beaker gently to loft the AgCl clumps slightly, and pour them, along with the solution, into the reserved centrifuge tube. The last of the precipitate may have to be washed in with MQ water.

Tap the base of the tube, working the AgCl into a compact mass at the base before centrifuging. If the tube is centrifuged immediately, AgCl flecks will spread over the floor, making it difficult to decant the liquid. Gathering the AgCl before centrifuging results in a small bead in the tip of the tube, which will not dislodge or wash away when the supernatant is discarded.

Centrifuge at ~2500 RPM for 5 minutes.

Decant off the liquid - the bead of AgCl will stick in the base of the tube.

Refill with 5 mL MQ water. Shake to resuspend the AgCl. Let it settle, gather it as before and centrifuge at 3000 RPM for 5 minutes. The bead will shrink noticeably.

Decant the rinse water and repeat. The bead will shrink further.

Don't rinse more than twice - after two washes the bead may fall apart when the rinse water is decanted off.

Dry the AgCl in its tube overnight in the Chloride Lab oven at 60 - 70°. (Lie the tube on its side so that water drains off the bead of AgCl).

(10) Storage

After drying, it should be possible to tap the bead of AgCl out of the tube in one piece, allowing it to be weighed for an approximate check on the yield.

Store it in its tube, capped tightly and wrapped with Al-foil, in a dark container. The AgCl should keep for many months without degradation. Exposure to light will result in gradual decomposition - formation of Ag metal (with loss of Cl₂) causes purple discolouration.

