

Environmental analysis – Digestion methods for geological materials

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The analysis of geological materials has been a core sub-discipline of the chemical sciences for more than a century. Analytical methods have evolved to become more rapid and sensitive. However, many of the preparatory techniques have only seen marginal development, largely due to the challenging natural properties of the materials under investigation. Related to this is the continuing need to work with potentially harmful reagents such as hydrofluoric and perchloric acid.

Historically, analysis of geological materials was carried out using classic wet chemistry procedures followed by gravimetric, spectroscopic or colorimetric quantification. Many of these methods still underpin more modern approaches, if only because of the continuing need to convert solid samples into liquids before their introduction into modern instruments.

Digestion using acids

Geological samples invariably contain silicate minerals for which dissolution requires the breakdown of the silicate lattice. The only acids readily capable of fully dissolving silicates are hydrofluoric acid (HF), combined with an oxidising acid such as nitric acid, a combination of nitric and hydrochloric acid as aqua regia, or perchloric acid. The risks to health and safety associated with these acids must be considered: HF whilst relatively weak ($K_a = 6.6 \times 10^{-4}$), has the potential to be extremely harmful because it causes the decalcification of bone; perchloric acid is a powerful oxidising agent when hot; and aqua regia, in addition to being a strong oxidising agent, will self-pressurise a containing vessel. Safer alternatives are being evaluated, most notably ammonium fluoride or ammonium bifluoride (1), but these are not risk free.

By far the best combination for open beaker digestions remains a combination of HF and perchloric acid (2), wherein HF readily dissolves silica to form SiF_6^{2-} , which is then lost from solution as SiF_4 gas. HF on its own is rarely used because of the potential to form insoluble fluorides such as CaF_2 . The relatively high azeotropic boiling point of perchloric acid (203°C) improves digestion efficiency and assists in the removal of SiF_4 . If

organic material is present in a rock sample, then initial digestion with nitric acid is recommended before the HF/ HClO_4 mixture is added. If a perchloric acid compatible fume cupboard is not available, then aqua regia can be substituted, although it is not as efficient. However, it can dissolve gold and other platinum group metals, which may not be fully digested with HF/ HClO_4 .

There are limitations associated with the approaches described above: the use of HF may result in the loss of volatile fluorides such as those of B, As, Ge and Sb (as well as Si), and the use of a chloride-containing acid under heat will result in at least the partial loss of Ge, Hg, Sb, As and Sn as volatile chlorides. To retain volatiles, PTFE 'bombs' or, more recently, a HF resistant sealed vessel within a purpose built microwave digestion system, have been investigated. The latter approach, although with a higher initial investment, has gained popularity because of its efficiency and ease of automation. Manufacturers advise against the use of perchloric acid in microwave digestion systems because of its violent reaction with organic compounds when hot and the risk of producing unstable perchlorate salts should a vessel part-fail and dry out during the digestion cycle; aqua regia or nitric acid are recommended instead. At the end of the digestion process, samples are cooled whilst sealed to encourage the condensation of volatiles, which are then removed by rinsing. This leaves the analyst with the challenge of dealing with an HF-rich solution and its associated safe handling challenges. Two options present themselves: either progress directly to an instrument with an HF-tolerant sample introduction and fume extraction system, or to complex the free HF with saturated boric acid. The use of boric acid increases the



Fused disc manufacture: molten flux and sample mixture poured from the crucible into the disc casting platen.

dissolved solids in the final solution (~2.8g of boric acid per 100mL of solution is used (3)) and, therefore, dilution is required prior to ICP analysis. Fluoroboric acid (HBF_4) is produced reversibly, and by increasing either the hydrogen ion concentration or the concentration of divalent cations, such as calcium, it is possible to hydrolyse HBF_4 and release HF (4).

A well-documented limitation of all acid digestion approaches is the challenge of dissolving acid-resistant mineral phases including rutile (TiO_2), tourmaline ($\text{Na}(\text{Mg,Fe,Mn,Li,Al})_3\text{Al}_6\text{Si}_6\text{O}_{18}(\text{BO}_3)_3(\text{OH,F})_4$), beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$), zircon (ZrSiO_4), chromite (FeCr_2O_4), and cassiterite (SnO_2), all of which are important repositories of key trace elements in geological samples. Whilst the heat and pressure of microwave digestion has improved matters, the challenge remains. This is exemplified by Potts *et al.* (5), who demonstrated that an uneconomically long (48 hour) HF-based digestion in a sealed bomb at 180°C was required to extract zirconium and related elements.

Whilst some geochemical studies invariably require the quantification of total elemental abundance, the use of partial digestions without HF are widely used in geoexploration and geoenvironmental studies on a fit for purpose, cost and safety basis. Modern microwave-assisted digestion systems are capable of digesting 40 or more samples simultaneously primarily using nitric acid, sometimes in combination with hydrogen peroxide, with aqua regia for metals in the platinum group (6).

Fusion-based preparation

Combining a small quantity of powdered sample with a flux, followed by heating in a platinum/gold (95%/5%) crucible, produces either a fused glass disc for analysis by X-ray fluorescence spectroscopy (XRF), or a solution for analysis via ICP. This is a core preparatory technique in the geosciences. Fusion fully breaks down most common geological minerals prior to instrumental analysis without the loss of silicon, including many samples that are resistant to acid, and it is therefore advantageous from a safety perspective. The use of small amounts of light element fluxes (e.g. 0.5g sample : 6.5g flux) overcomes the limitations of using pressed pellets of rock powder in XRF, where critical penetration depth effects and absorption/enhancement of the X-ray signal perturb results. Because of dilution effects and the sensitivity of XRF instruments, fused discs tend to be used for quantification of the most abundant elements samples. Pressed pellets are used for the determination of elements present at lower concentrations, typically less than 0.1 wt %, and careful matrix matching between standards and samples is required. Fused disc production is readily automated and takes approximately 20 minutes using a modern fusion instrument. Flux composition may be dependent upon sample type (7). Our laboratory routinely uses a 50:50 mixture of lithium metaborate and lithium tetraborate combined with a small amount of lithium bromide to act as a non-wetting agent for the platinumware.

Because of advances in the sensitivity of ICP-based analytical techniques, allowing quantification of elements such as the lanthanides, flux and sample solution has proved useful in producing diluted samples that reduce the risk of 'salting up' the nebuliser. We routinely quantify 50 elements this way, and achieve excellent results in proficiency testing round robin evaluations. The flux usually consists of lithium metaborate mixed in a 5:1 ratio with the sample powder. The molten, fused mixture is poured hot into a quantity of stirred, dilute nitric acid, causing the fused bead to shatter and dissolve within 30 minutes. Some automated fusion instruments can be modified to produce fusion-based solutions instead of fused discs; for simplicity and economy, we fuse samples in pressed graphite crucibles heated in a muffle furnace. This approach generates 36 fusion solutions per day. The approach precludes the quantification of volatile elements such as mercury, arsenic and cadmium.

At low abundances, noble metals may be quantified via the related nickel sulphide fire assay technique (8). The pellet from this preparation is typically dissolved in acid and analysed with ICP, negating the need for the less common quantification by neutron activation analysis.

Whilst no one preparatory method provides the 'silver bullet' for quantification of all geochemically important elements, improvements in the sensitivity of analytical techniques have allowed analysts to quantify elements at ever lower concentrations, providing stricter standards of cleanliness are adhered to in the laboratory and higher purity reagents used. Nevertheless, geoscience reference materials must be included alongside unknown samples to validate the chosen prep method and sampling strategy remains critical.

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