

# Gamma activation analysis

## A new gold standard?

BY **DAVE SAMMUT**

**A gold assay developed by CSIRO Minerals may avoid interferences that frustrate current methods.**

**F**irst discovered in the Australian colony in 1823 by Government Surveyor James McBrien, gold has played a huge role in the development of Australia as a nation. It wasn't the first mineral mined or exported from Australia – by 1823, more than 3000 tonnes per year of coal was being mined and hand-loaded by convicts into ships at the port of Newcastle – but it played a major role in defining the country we live in today.

In 2014, Australia was the world's second largest producer of gold (after China), producing over 270 tonnes of the yellow metal. Mined in almost half the countries of the world, gold had a global production in 2014 of 2860 tonnes, according to the US Geological Survey.

The dominant gold assay method at present is fire assay. A known quantity of crushed ore (usually 30–50 grams) is mixed with flux in a refractory crucible. The flux is typically a mixture of sodium bicarbonate, potassium carbonate, sodium borate, lead oxide and either flour or iron metal as a reducing agent, depending on whether the ore is an oxide or a sulfide.

The mixture is heated to 1000–1200°C. Via a complex series of reactions that depend on the sample chemistry, the lead is reduced to a 'button' of metal alloyed to the precious metals in the sample, while the remainder separates as a slag.

The lead buttons are put into porous crucibles made of 'bone ash' (MgO), termed 'cupels', which are then reheated to 1000°C in a muffle furnace under oxidising conditions. The lead melts and oxidises to PbO, which in turn melts and is drawn into the pores of the cupel by capillary action. The gold remains in the base of the cupel as a 'prill', which is then assayed for metal content.

Fire assay is a time-consuming, destructive technique. The accuracy is limited to around 5% for typical ore samples, on top of the error rate in the sample preparation (see box). Yet such is the demand from gold (and platinum group metals) exploration and mining that Australian laboratories collectively produce as much as 100 tonnes per month of lead-contaminated cupels as hazardous waste.

CSIRO has introduced a potentially game-changing assay technique –



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gamma activation analysis (GAA). Much less labour intensive, and with no hazardous waste, it should enable detection of all of the gold in a sample, regardless of the chemistry or matrix. DCS Technical spoke to Dr James Tickner about CSIRO Minerals' work on this new analytical method.

CSIRO's GAA testing uses a high-power electron linear accelerator (LINAC) X-ray source developed by Mevex Corp Ltd of Ottawa, Canada. It produces an electron beam of around 8.5 MeV directed onto a water-cooled copper target, which produces X-rays via the Bremsstrahlung process. Samples are placed in 300 mL containers positioned close to the target. The electron beam is rastered over a calculated path on the copper



## Sampling challenges

Gold is only very sparsely dispersed through the Earth's crust. The average gold grade for operating gold mines in 2012 was only 1.06 g/t (1.06 ppm) ([bit.ly/1LQJKZQ](http://bit.ly/1LQJKZQ)). Even the average for the world's top ten mines was only around 15 g/t in that year ([bit.ly/1GMz1AW](http://bit.ly/1GMz1AW)). And these figures are the averages for the *ore* itself, before recovery efficiencies are taken into account for the beneficiation of the ore into concentrate, and the extraction of the gold from the concentrate to metal (typically via cyanidation).

Overall, this means that for every tonne of gold produced, these mines drilled, blasted, carried, crushed and processed more than one million tonnes of host rock, plus uncounted millions more of 'overburden', the valueless spoil that has to be removed before the mines even get to the ore.

From an analytical chemists' perspective, the challenges in this endeavour are huge. Finding one gram of gold dispersed through a tonne of material is very much 'needle in a haystack' territory.

The gold may be either widely dispersed or 'nuggetty' within the sample; the latter gives extremely heterogeneous samples. Due to its high relative density, gold often separates via simple movement under gravity. This property can be a major advantage for the beneficiation via shaking tables, spiral or rotary classifier, or simply by panning for amateur enthusiasts, but requires careful attention during sample preparation for assaying.

After the initial challenge of getting a representative sample from some tonnes of coarse source material, the operator needs to crush and homogenise the sample, then sub-sample via riffle splitting or classic 'cone and quarter' methods. A key problem with this is that good sampling requires skilled operators, and results are therefore subject to random and operator-based error.

to ensure uniform irradiation of the sample.

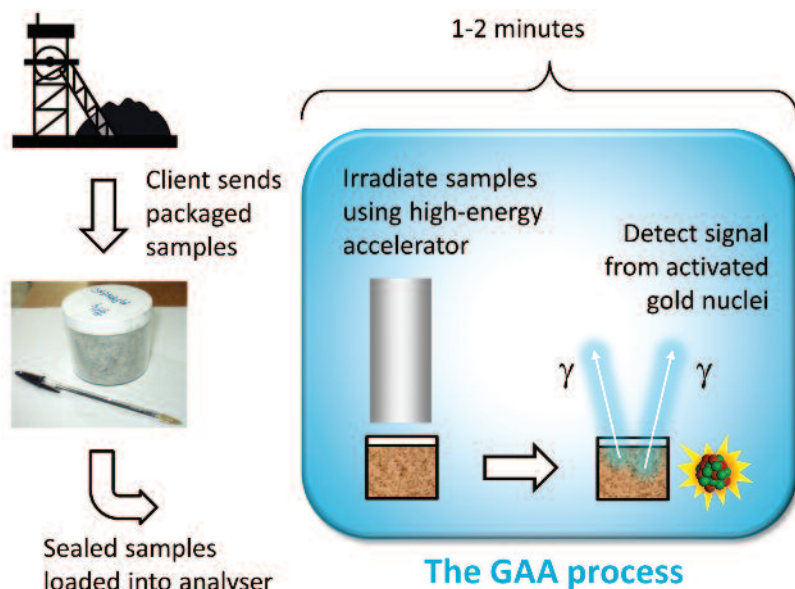
Tickner notes that there is no simple distinction in energy between X-ray and gamma radiation. Instead, the convention is that 'X-ray' refers to radiation generated electrically, while 'gamma' refers to energy from nuclear reactions. GAA is then so-named for historical reasons, with intense, high-energy gamma-ray sources being initially used.

Bombarding the sample with high-energy X-rays induces nuclear reactions in the elements of the sample, and the resulting isotope decay reactions generate characteristic gamma rays that can be compared to standard samples for quantified elemental analysis.

For gold analysis, the most important reaction is the excitation of the 409 keV, 7.73 second half-life isomeric state. This half-life allows the sample to be moved between the irradiation and measurement zones, protecting the liquid nitrogen-cooled germanium detectors from the intense radiation required to excite the isomer.

A 'monitor foil' is used to correct for variations in the X-ray flux from the source, or changes in detector efficiency. This is simultaneously irradiated and measured with the sample. If done correctly, both are subject to nearly identical changes in activation, allowing normalisation of any variation in the analytical factors.

Following irradiation of the sample, the decay gamma rays are measured



and related back to the gold concentration via the sample mass. A Monte Carlo simulation is used to calculate a mass/density correction factor, which Tickner reports as giving surprisingly high accuracy in the correlations, in the region of 1%.

Tickner says that the technique is not entirely novel. Originally suggested as a possible gold analysis method in the 1960s by groups in the US, the method was first applied in an industrial setting in the 1970s in the former Soviet Union. Unfortunately, details available in the English language literature are limited.

GAA has commonalities with both X-ray fluorescence (XRF) and neutron activation analysis (NAA). Like XRF, GAA uses incident X-ray radiation. However, whereas XRF induces only energy shifts in the electrons to measure the resulting releases on the return to ground state, GAA induces much larger changes at the nuclear level. Essentially, the higher energy X-rays of GAA blast neutrons out of the nucleus, or cause shifts between nuclear energy levels, producing unstable nuclei that subsequently decay.

NAA similarly induces nuclear reactions in the target elements by

adding (nuclear reactor generated) neutrons to the nuclei. However, the technique is relatively unselective, as many common rock-forming elements are capable of absorbing neutrons and becoming radioactive. This creates a large background of gamma radiation across the energy spectrum and therefore reduces sensitivity. Typically, samples must be left for a long time

(usually more than seven days) to allow this background to decay before sensitive measurements for trace elements such as gold can be performed.

By using electrically generated X-rays, GAA is able to 'tune' the incident energy to target the desired elements. This works particularly well for gold, which activates at lower energy than

### 'Invisible gold'

There is a niche but persistent concept in gold circles termed 'invisible gold'. Put simply, this is gold that, for various reasons, is supposedly present in samples but simply doesn't show up in conventional fire assay techniques, or by acid digestion and spectroscopic analysis.

In theory, it is certainly at least conceivable. If gold were locked in refractory particles, particularly if that gold were encapsulated at the nano-scale so that none was exposed at any particle surfaces, perhaps it might not be available for any of the chemically based analyses. If it can't react or dissolve, then it can't be measured by any of the existing techniques.

GAA may answer this question once and for all. Free from matrix effects and chemical reactions, GAA comes down to the pure physics of the sample. If it is present, then the atoms should be activated and the resulting isotopes should decay.

In the interview with DCS Technical, Dr James Tickner of the CSIRO noted that the technique had been trialled on several purported invisible gold samples. For those samples, he concluded that the gold 'was indeed invisible'. He went on to state that 'If the gold does not show up in a brute force nuclear reaction, then [if it were actually present] this would require a Nobel Prize-winning change to our understanding of physics.'



A typical gold mine would drill ten kilometres or more diamond drill cores such as these each year.

many other elements. And by avoiding activating many background elements, the sensitivity of the technique can be improved.

Tickner explains that GAA is applied at a high-grade mine in Uzbekistan based on the old Soviet work, apparently achieving a 0.5 ppm detection limit. Using the newer high-energy X-ray sources developed for the medical sterilisation and industrial radiation markets, and improved detector systems, Tickner and the team are aiming for limits in the low tens of ppb.

Despite the high energies of the source X-rays, the resulting isotopes have very short half-lives. This yields rapid measurements, in the order of around 1–2 minutes, rather than the 30–60 minute measurements typical to NAA. This also means that the technique is non-destructive, which could be of particular benefit to the mining industry. During exploration, each metre of core can cost thousands of dollars to obtain, and with only

limited quantities available, the samples can have multiple uses.

GAA uses much larger samples than fire assay, typically around 500 grams. This has the potential to reduce the effects of sampling error (by averaging out variation to some extent). Interestingly, the quantity is not defined by mass itself, but by the fixed volume of the sample container.

The technique has the advantage over XRF that the higher-energy incident and decay radiation largely removes matrix interferences: particle size, packing density and sample distribution.

Free from the requirement for a nuclear reactor to generate the high-energy source, Tickner envisages that GAA could become a portable technique. However, 'portable' is in this case a relatively loose term. With the required shielding and equipment, a single unit could be the size of a shipping container. Even so, this offers potential advantages for field use in minerals exploration.

To date, the CSIRO team has concentrated its efforts on gold, having tested a wide range of samples in summer campaigns at Mevex Corp's facility in Canada. This has included ores, concentrates, tailings and carbon samples (from  $CN^-$  processing), with the typical range of sulfides, oxides and silicates.

The work has concentrated on investigating and refining the technique, with a particular emphasis on the subtleties of the density correction. Tickner now has his eyes set on establishing a commercial analysis facility in Adelaide, probably in 2016–17. Likely costs associated with this method, which may be the main potential disadvantage, have not yet been disclosed. I'll be keeping a close eye on this for my consultancy's gold samples.

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## GAA across the periodic table

Approximately half of the periodic table will respond to gamma activation. However, although weighted towards higher atomic numbers, the response is not linear. Adjacent elements can have quite different activations, and it is therefore fortuitous that the technique is so well suited to an element as commercially important as gold.

Fortunately for the mining industry, other key commercially relevant elements are also well suited to GAA. Copper offers a strong activation that is both easy to observe and measurable across the useful commercial range of concentration.

Silver and lead are straightforward, and while zinc is somewhat more difficult, it is still measurable with GAA.

Platinum group metals are measurable, but less sensitive than gold due to higher energies of activation and resulting greater difficulty of separating background radiation from co-activated elements, particularly given the typically low concentrations of platinum group metals in samples. As such, for now GAA will probably be more suited to platinum group metal concentrates and metal accounting, rather than ore samples.

Rare earths, uranium and thorium are accessible by GAA. Higher energy X-ray sources will be required before iron will become practical for precision work.

For gold analysis, key interferences are elements such as Ba, Br, U and Th, which fission at low energy, pushing up the background and reducing sensitivity. However, interference typically occurs at closer to the per cent level, which is not common for those elements in commercial mineral samples.