Application of PhotonAssay™ to Coarse-Gold Mineralisation – The Importance of Rig to Assay Optimisation

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1. Introduction

1.1 The Importance of Sampling

Sampling errors are additive throughout the complete lot-toadditive aliquot sampling value chain and can generate both monetary and intangible losses (Carrasco, Carrasco & Jara, 2004; Minnitt, 2007; Dominy, 2016; Lyman & Bourgeois, 2017; Lyman, 2019; Pitard, 2019; Esbensen et al., 2021). Sampling, inclusive of collection, preparation and assaying is a vital component of all stages of a mining project (Minnitt, 2007; Dominy, 2016; Lyman & Bourgeois, 2017; Pitard, 2019; Esbensen et al., 2021). This includes the sampling of in-situ material and broken rock for geological, metallurgical, geometallurgical and geoenvironmental purposes.

Field sampling is followed by sample reduction in both mass and fragment size to provide sub-samples for testwork or assaying. This process can be particularly challenging in the precious metal environment (e.g. gold and platinum). Sampling

errors are defined in the Theory of Sampling (TOS) (Gy, 1982; Pitard, 2019; Esbensen, 2020). These errors are relevant to all applications across metallurgy, resource evaluation and grade control. To undertake representative sampling, practitioners need to

ABSTRACT

Sample collection, preparation and assaying are a vital activity at all stages of a mining project. Field sample collection is followed by sample reduction in both mass and fragment size to provide a sub-sample for assay. This process can be particularly challenging in the precious metal environment and may require specifically designed protocols. One of the biggest challenges is ensuring that all sampling and subsampling errors are controlled across the entire rig to assay pathway. In most cases, the primary sampling error (the error at the rig and/or core shed) may swamp the entire process. Challenges also exist throughout all sampling stages when coarse gold is present. In particular, the pulp is likely to contain some liberated, poorly comminuted gold particles, requiring the pulp to be assayed in total to avoid unnecessary additional errors during splitting and handling. PhotonAssay™ is a non-destructive and rapid gold assay technique capable of analysing coarse crushed (<3 mm) 350-500 g samples at a rate of ~70 samples per hour. It displays fast assay turnaround-time, requires lower staffing levels to operate, and removes the need for chemicals such as lead or cyanide. These characteristics make it applicable to gold ores, particularly those bearing coarse gold, as only crushing is required (minimal liberated gold) and multiple lots can be assayed. However, this advantage will be reduced if any of the sampling stages are not optimised. The optimisation of a sampling protocol comes from understanding the mineralisation and desired programme outputs. It is not simply a mathematical, or a statistical process, but a complex process taking advantage of orebody knowledge (including gold deportment studies) and application of the Theory of Sampling.

optimise field sampling to assay protocols by undertaking characterisation of the mineralised domains present (Minnitt, 2007; Dominy, 2016; Villanova, Heberle & Chieregati, 2017; Dominy et al., 2021; Dominy, Glass & Purevgerel, 2022).

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TOS can be applied to optimise sampling of all types of stationary and dynamic lots as well as for comprehensive analysis of manufacturing and processing variabilities. TOS is the key factor to identify solutions with improved efficiency and the only effective tool for guarding against unnecessary economic and material losses.

1.2 Rationale for this contribution

Given the novel nature of PhotonAssay™, this contribution provides a summary of the technique and presents the key areas that the Competent/Qualified Person (CP/QP) must consider before implementing any changes to an existing protocol and/or introducing a new one. Key matters pertaining to the sampling of coarse gold mineralisation are also discussed. The paper is based on the experiences of a group of practitioners – some of whom are CP/QPs – who have extensive experience of the implementation and application of PhotonAssay™ across the mine value chain. The utility of PhotonAssay™ and the importance of "rig-to-assay" optimisation are exemplified through four case studies.

1.3 Peculiarities of Gold Sampling

1.3.1 Overview

There are several peculiarities of sampling for gold, which relate to both correct (CSE) and incorrect (ISE) sampling errors. For the definition of the TOS errors refer to Appendix Table A1 and for abbreviations used in this contribution Table A2.

The main influential drivers for the fundamental sampling errors (FSE) include:

- Primary gold particle distribution is often erratic (high geological nugget effect), with localised clustering effects (Dominy & Platten, 2007); and
- Grades are low (g/t Au), thus gold particles can be rare 'events' (e.g. Poisson distribution) particularly in low grade ores (Pitard & Lyman, 2013).

Those issues that contribute to the grouping and segregation error (GSE) and ISE include:

- Poor disintegration of gold particles during pulverising often lead to smearing and/or the coating of sample preparation equipment leading to PE (Royle, 1989; Dominy & Petersen, 2005; Dominy, 2017; Pitard, 2009); and
- Extreme contrast between the densities of gold and gangue minerals promote segregation once liberated which contributes significantly to GSE (Pitard, 2019; Minnitt, 2022; Minnitt, Dominy & Esbensen, 2022).

These problems can partly be reduced, but not eliminated, by using larger sample and assay charges in combination with careful procedures to minimise all sampling and sub-sampling errors.

Gold mineralisation often contains both fine (<100 μ m) and coarse (>100 μ m) gold particles. The in-situ size and shape, deportment, distribution and abundance of these particles controls deposit sampling characteristics, grade distribution and metallurgical properties. Gold particle sizing can range from individual disseminated, to clusters of particles, through to centimeterscale masses. From a sampling perspective, mineralised domains can possess varied gold particle size characteristics.

Mineralisation containing substantive quantities of coarse gold (>15% above 100 μ m) is often typified by a high geological nugget effect which represents variations in (1) the in-situ size distribution of gold particles (including the effects of gold particle clustering), and (2) gold particle abundance (Dominy & Platten, 2007; Dominy, Platten & Xie, 2008; Dominy, 2014). Where the sampling process is not optimised, the sampling nugget effect (SNE) is enhanced, increasing the total nugget effect (Francois-Bongarcon, 2004; Dominy, 2014).

1.3.2 Challenge of gold content and successive splits

The gold content of an extracted sample and the gold content of the surrounding mineralisation *can* be vastly different. Similarly, there may be significant differences between the primary sample, subsequent subsamples and the final fire assay (FA) charge unless rigorous procedural optimisation is undertaken. FA is the traditional method for gold assay (Hoffman, Clark & Yeager, 1999).

Skewed/non-normal distributions of assays arise from low primary sample masses and/or from insufficient pulverisation of material and assay charge mass. For mineralisation in each state of comminution, the true grade of a sub-sample will differ from that of the original 'lot'. If sub-sampling is conducted in an unbiased correct manner, the actual assay difference will be due to the size and grade distribution of the gold particles in the lot and the nominal mass of the sub-samples.

Mineralisation dominated by fine gold may be broken to a particular size distribution with the gold particles spread throughout the host rock. There will be no gold particles that are fully liberated. The distribution of gold within particles will be confined to low values that may reach a few hundred g/t. In this case the assay distribution within any of the size fractions is likely to be unimodal.

In the case where the gold particles are coarse, comminution will liberate some of the gold. In this case a given size fraction will contain both liberated gold and fine-disseminated gold in rock fragments. The liberated gold particles will bear very-high grades (into 1,000's g/t Au), which will form a distinct peak in the grade distribution. The grade distribution will be bi- or multi-modal, reflecting populations of fine disseminated gold and coarse liberated gold.

Gold particle clustering on the millimeter to centimeter scale may have a large effect on the block-to-hole, hole-to-sample, and sample-to-assay representativity (Dominy & Platten, 2007; Dominy, Platten & Xie, 2008, 2021; Dominy, Glass & Purevgerel, 2022).

There follows two examples on how the sample protocol applied can affect the final assay.

Example No. 1

Consider a 1 m length of NQ2 drill core of weight c. 6.4 kg. The true assay of the core is 10 g/t Au. The core contains c. 64 mg of gold. Assume 12.5 mg occurs as 10 coarse particles of 500 µm diameter (coarse gold component of grade is 2 g/t Au), with the remaining 51.5 mg as small numerous <100 µm particles that pose no sampling issues. If the entire core is crushed to P_{80} -2 mm and a 1.2 kg (1:5) split taken correctly, then the expected number of coarse gold particles is 2. However, the probability of collecting two particles is only 30%. If the first split yielded an assay of 11 g/t Au (20% probability; N = 3), there are 7 coarse gold particles left in the remaining 5.2 kg residue. Based on 90% confidence limits, the likely number of particles collected will be between 0 and 2, and the split grade will lie between 8 g/t Au and 10 g/t Au.

If either 1.2 kg split is pulverised, where it is assumed that pulverisation is incomplete with substantial coarse gold left and not reduced in size, then the probability of collecting zero coarse gold particles is >95%, with a resultant gold grade of 8 g/t Au. There is a 4% probability of encountering a single gold particle, but in a 25 g FA charge this will yield a grade of 58 g/t Au. If pulverisation were more efficient, the probabilities of finding 0, 1, 2, etc. particles would be the same, but the assays would change where there is more disseminated gold and less coarse gold.

Example no. 2.

Pitard & Lyman (2013) provide a similar study, where a 3.84 kg length of NQ half core was pulverised in its entirety and assayed to extinction via 128 30-g FA. The mean FA grade was 2.31 g/t Au, with the range of FA being 0.36 g/t Au to 63 g/t Au showing a coefficient of variation (COV) of 328%. Some 88% (113) of the FA values understated the true mean of 2.31 g/t Au. Pitard and Lyman (2013) calculated that the mean coarse gold particle size in the lot was 743 µm. Therefore, the average number of gold particles in a 30 g FA was 0.045, or 1 in 22 FA. The probability of a 30 g FA selecting no coarse gold was 96%; of selecting a single particle was 4%; and two particles 0.1%.

Both these examples highlight the marked challenge of using a 30 g FA charge in the presence of coarse gold and the likelihood of a highly skewed grade population resulting. These analyses reiterate the fact that where the pulverising process is inefficient, assays provide for the appearance of 'erratic' mineralisation. A well-pulverised pulp need not be a guarantee of correct sample preparation; the assay of the crushed rock submitted to the pulveriser may already bear no resemblance to that of the original sample. Similarly, well-behaved pulp duplicates need not imply an efficient process either if a key part of the gold particle population has a high probability of not being selected in the rig to pulp path. It is critical where in the compound rig-to-pulp pathway changes in pulverisation efficiency and monitoring is brought to bear, for example by duplication. The systematic use of replication as a QAQC vehicle is discussed in Abzalov (2008), Esbensen (2020) and Dominy, Purevgerel & Esbensen (2020).

While grade is often correlated to gold particle size and abundance in the sample, the relationship between sample grade and the surrounding ore is complex (Dominy & Platten, 2007; Dominy, Xie & Platten, 2008). High grades (>15 g/t Au) often relate to abundant coarse gold and/or clustered gold particles which, by virtue of their high-grade, may not be too challenging to sample. Interpretation of samples containing coarse gold-bearing low-grade (<5 g/t Au) mineralisation is challenging. The sampling and preparation of coarse gold mineralisation is discussed further in Royle (1989), Dominy et al., (2000), Johansen & Dominy (2005), Petersen & Dominy (2005), Cintra et al., (2007), Dominy (2014, 2017), Clark & Dominy (2017) and Dominy, Glass & Purevgerel (2022).



Fig. 1: PhotonAssay[™] unit at Intertek Perth.

2. PhotonAssay™ Assay Technique

2.1 Introduction

The PhotonAssay™ method is a new non-destructive, rapid gold assay technique capable of analysing coarse (optimally <3 mm) 300-500 g samples at a rate of ~70 samples per hour (Figure 1; Tickner et al., 2017; Tickner, Preston & Treasure, 2018; Tremblay et al., 2019; Tremblay, Wheeler & Oteri, 2019; Tickner, 2021). Each PhotonAssay™ unit has the approximate dimensions of 6.1 m (W) by 7.3 m (D) by 2.7 m (H) and weighs 80 t.

The science behind PhotonAssay™ was developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO) in Australia, and the technology was developed and commercialised by Chrysos Corporation. Initial roll-out and validation was conducted in partnership with commercial laboratory groups.

The method is lead and cyanide free, hence adding substantial health and safety advantages. It can be widely applied across the full mine value chain inclusive of exploration (drilling and reconnaissance sampling), resource development (reverse circulation – RC and core drilling), grade control (RC and core samples; stockpile samples; underground samples), metallurgical testwork (head, tails and concentrate samples, and ore sorter testwork) and plant control (feed, process, solutions, carbon, concentrate and tails samples).

The method has also proven to be of utility during ore sorter testwork programmes, where it can be used to assay multiple samples of rejects and concentrates.

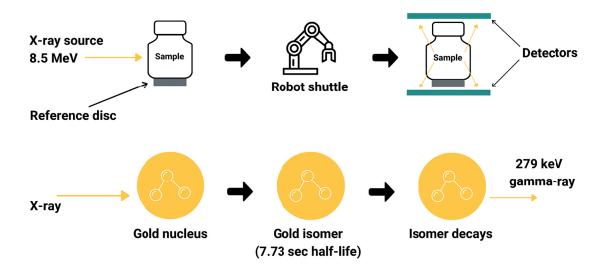


Fig. 2: Illustration of the PhotonAssay™ process.

2.1.1 PhotonAssay™ Technology

Based on the principles of *photon activation analysis*, the method uses a high-power, high-energy X-ray source to excite nuclear changes in any gold atoms present in a sample, followed by measurement of a characteristic signature emitted by these atoms (Figure 2).

Sample material is loaded into a sealed plastic jar in which it remains throughout the analysis (Figure 3). A removable reference disc is fixed to the outside of the jar.

The sample and reference disc is exposed to the same high-energy, high-intensity X-ray beam, typically for 15 seconds.

The high-energy X-rays induce nuclear changes in any gold atoms present in the sample, exciting their atomic nuclei into a short-lived state. When gold nuclei in the sample absorb the high energy X-ray photons created from the LINAC they are transformed into the 197mAu nuclear isomer. This species decays with a half-life of 7.73 seconds and emits a gamma ray of 279 keV.

The sample is transferred to a germanium detector station using a robotic shuttle. As the excited gold nuclei relax back to the ground state, they emit gamma rays with a characteristic 'gold energy'. The detectors record and count these gamma rays.



Fig. 3: Illustration of PhotonAssay[™] process from left to right: sample jar registration and jar fill scanning; automatic feed of sample jars into the unit; and automatic outflow of jars from the unit.

Software then relates the strength of the gamma ray signal back to the concentration of gold in the sample, correcting for the sample mass, jar fill level and X-ray attenuation. The standard assay process is based on two cycles (PAAU02; Chrysos, 2022a), where the sample jar is irradiated twice (15 s each time) with the two values averaged to provide the reported grade. The basic flow of sample jars into the PhotonAssay™ unit is illustrated in Figure 3.

The reference disc contains a compound of the element bromine, which activates in a similar fashion to gold, but emits a lower energy 207 keV gamma ray. Measurement of the bromine activation signal serves as a reference that can be used to correct for any variations in the power of the X-ray source or efficiency of the detection system. This reference significantly improves measurement accuracy and allows each analysis to be directly tied back to calibration measurements performed on a suite of certified reference materials (CRM). This technique is relatively insensitive to assay material granulometry, thus rock chips or larger rock fragments can be measured. It is also insensitive to the sample matrix, so different rock types, process materials, solutions and carbon pulps can also be assayed.

X-ray levels outside of the unit are low so that operators can work safely without the need for special precautions. The short irradiation period and jar retention within the unit for two hours after measurement, ensures that residual sample activity is minimal. Jars can be safely handled, stored and/or reused as required.

2.1.2 PhotonAssay™ Parameters

The PhotonAssay™ measurement precision at one standard deviation (1SD) varies with grade (Table 1; Chrysos, 2022a). The lower detection limit (LDL) at 2SD is approximately 0.02 g/t Au to 0.03 g/t Au for typical samples. The upper detection limit is 350 g/t Au, though can be increased to 10,000 g/t Au as required (PAAU02H and PAAU02HH; Chrysos, 2022a). The above figures are based on the standard two-cycle assay process (PAAU02; Chrysos, 2022a).

Enhanced PhotonAssay™ performance can be achieved via the four- and eight-cycle assay process, where up to 1.4x and 2x improvements of the two-cycle LDL and precisions can be gained. The increased cycles take longer to complete and attract additional cost. For most purposes the two-cycle process is approriate and cost effective.

The PhotonAssay™ methodology is relatively matrix insensitive, although significant levels of uranium, thorium, barium and lead decrease precision and increase the detection limit. Samples with uranium—thorium levels >5 ppm, barium >1,000 ppm and lead >2% start to show these effects, although gold can be measured in samples with much higher levels of these elements. Higher concentrations of interfering elements may not preclude assay, depending on needs.

In addition to gold, PhotonAssay[™] can also determine silver and copper. Silver can be measured in the 1–2 g/t Ag to 10,000 g/t Ag range, and copper up to 30%.

Tab. 1: Performace parameters for fire assay compared to PhotonAssay[™] (PAAUo2).

Gold assay performance	Fire assay	PhotonAssay
LDL	0.005 g/t [ICP] 0.01 g/t [AAS] 0.05 g/t [gravimetric]	0.02-0.03 g/t
UDL	350 g/t Au [ICP] 100 g/t Au [AAS] 10,000 g/t Au [gravimetric]	350 g/t [PAAU02] 3,500 g/t [PAAU02H] 10,000 g/t [PAAU02HH]
Precision at 0.1–0.2 g/t Au	10%	10%
Precision at 0.35 g/t Au	5-8%	7%
Precision at 1.0 g/t Au	3-7%	4%
Precision at >10 g/t Au	2.5-3.5%	2.5%

The environmental impact parameters of PhotonAssay[™] are an improvement on FA, where CO₂ emissions are 0.45 kg (0.91 kg for FA), hazardous waste is zero (0.31 kg for FA), and energy use is 0.65 kWh (1.3 kWh for FA) per assayed jar. Compared to FA, PhotonAssay[™] is much quicker taking two to three minutes per jar compared to three to four hours.

2.1.3 PhotonAssay™ Calibration

PhotonAssay™ units are calibrated via the "k-cal" process at the start of each day or after a significant break in machine operation. Three jars containing synthetic crushed glass are run through the machine for 8 cycles each. The different glasses used in the jars have gold grades in the range 50-150 ppm. The glass is specially manufactured for Chrysos and was chosen because it is chemically and mechanically stable, not prone to settling, easy to manage and to transfer to new jars as required, and non-hygroscopic. However, it is not a certified material and must be calibrated before use.

2.1.4 PhotonAssay™ Data Outputs

Grade data from PhotonAssay is delivered via the relevant laboratory information system in an agreed format (e.g. .csv and/or PDF). Data generally provided includes: sample number, gold grade, assay error, and weight of sample in the jar. Specific codes may accompany a given result. The most common ones being: BDL (below detection limit); HB (high background related to high U, Th or Ba content); HET (heterogeneous sample related to high within sample variability); OVR (overlimit where the grade is above the upper limit of the measurement range — e.g. 350 g/t Au for PAAU02); IS (insufficient sample where the jar fill factor is <50%); and IE (interfering elements which could be Br or Er).

2.1.5 PhotonAssay™ Units in Operation

As of 30 September 2023, there were 22 PhotonAssay™ units deployed across the globe based in Australia, Africa and Canada (Chrysos, 2023b). A further 27 units are commercially contracted out to 2025 (Chrysos, 2023b).

Commercial laboratory operations include ALS, Perth and Kalgoorlie, Australia; Intertek, Perth, Australia; On-Site Laboratory Services, Bendigo, Australia; MSALABS, Prince George, Val d'Or and Timmins Canada; and SGS, Perth, Australia.

These laboratories cover regionally important goldfields in Western Autralia; The Golden Triangle of BC, Canada; Abitibi Province of ON, Canada; and West Africa.

Early movers in the global mining industry to use PhotonAssay™ include Agnico Eagle Mines Limited (Fosterville mine, Australia), Barrick Gold Corporation (various global operations), Goldfields Ltd (Australia), Firefinch Limited (Morila mine, Mali), Newfound Gold Corporation (Queensway project, Canada), Northern Star Limited (various projects in Australia), Novo Resources Corporation (Beatons Creek and exploration projects, Australia), Alto Metals Ltd (Sandstone project, Australia) and Ravenswood Gold Limited (Ravenswood mine, Australia).

2.2 When Should the PhotonAssay™ Technique be Applied?

The choice of any sample preparation and assay protocol is up to the CP/QP based on consideration of the mineralisation in question and data quality objectives. The ultimate destination of the output data is also critical. In most cases this will be publicly reported and potentially included in Mineral Resource and Ore/Mineral Reserve estimates to be reported in accordance with one of the international codes (e.g. JORC, CIM, PERC, etc.). The key assay options are given in Table 2.

In theory the PhotonAssay[™] technique can replace any of the methods listed in Table 2. However, there are over-rides for distinct reasons. If an investigation of the presence of coarse gold is required, then the SFA is valid, though PhotonAssay[™] can be used to assay the SFA oversize and undersize. Where a proxy for cyanide metallurgical recovery is required, then LW or PAL are required. If mapping of gravity recoverable gold is required, then the SFA or GRAV approaches will be needed, though PhotonAssay[™] is suited to the assay of residues from this process. If a large assay mass is applied (e.g. multiple PhotonAssay[™] jars), then the variability of the jar group (e.g. 10 jars) may be correlated with gold particle size and gravity recoverable gold potential (Dominy & Graham, 2021).

In some cases there may simply be no advantage of changing to PhotonAssay $^{\text{TM}}$ as the current method is performing well and/or the laboratory setup is costeffective, convenient and provides the required data quality objectives.

Tab. 2: Summary of gold assay methods.

Assay type	Assay charge	Nature of method	Application	Outcome
Fire assay (FA)	30-50 g	The standard method of fire assaying for gold	Small charge mass. Poor reproducibility in the presence of coarse gold	Grade
Screen fire assay (SFA)	0.5-5 kg	A variant of FA, the SFA reduces the coarse-gold problem by sieving out the coarse fraction (100-150 µm screens) and assaying it separately	An effective method for dealing with coarse gold. Can be used on samples up to 10 kg	Grade Per cent coarse gold
LeachWELL (LW)	0.5-5 kg	The method overcomes the problem of coarse particles by assaying the entire sample. 6-24 hours leach time effective for most coarse gold deposits	Large charge mass. Effective method for dealing with coarse gold. The method needs to be controlled by assaying the undissolved residues to check for partly dissolved gold	Grade Proxy leach recovery (if tails assayed)
Pulverise and leach (PAL)	0.5-1 kg	Essentially same as Leach – WELL. Crushed (approx. P ₈₀ –10 mm) sample is leached and pulverised at the same time 1–1.5 hour leach time	Smaller charge mass. Potentially effective method for dealing with coarse gold. Some issues relate to contamination of pulverise/leach pots. Method needs to be controlled by assaying the undissolved residues to check for partly dissolved gold	Grade Proxy leach recovery (if tails assayed)
Whole sam- ple gravity processing	>50-500 kg	Takes large sample and processes entire via gravity (e.g. Knelson and/or Wilfley table) to produce a gold concentrate and tails for assay. 8-12 hours or more	Large charge mass. Effective method for dealing with coarse gold. Method needs to be managed to ensure maximisation of gold recovery Not useful for fine gold, unless gravity used for gold-rich sulphide concentration and/or clustered fine gold is present, hence larger sample warranted	Grade GRG (single or 3-stage) Proxy leach recovery (if tails leached) Gold particle size profile (if GRG screened)

Tab. 3: Sampling value chain. Refer to definitions of TOS errors in Appendix Table A1.

Location		Site / field			aboratory
Node	Planning	Collection	Transport	Preparation	Assaying
Activity	Characterise Design Implement Write protocols Staff training	Observe Collect Bag and tag QA/QC Integrity/security Chain of custody	Integrity/security Chain of custody	Equipment operation Equipment clean QA/QC Integrity/security	Equipment operation Equipment clean QA/QC Integrity/security
Sampling	error	FSE, GSE IDE, IEE, IWE	IPE	FSE, GSE IDE, IEE, iWE, IPE	FSE, GSE IDE, IEE, IWE, IPE
Dominant	effect on results	Precision Bias	Bias	Precision (if splitting) Bias	Precision (if splitting) Bias

2.3 General Considerations of Using PhotonAssay™

2.3.1 Setting up a Programme

The same consideration for any drilling, sampling and assaying programme is relevant to the application of PhotonAssay™. All aspects of the sampling value chain must be considered, where all nodes of activity require optimum practice to ensure representative samples to support quality assay results (Table 3).

Discussions of the pros and cons of various drilling and sampling methods are provided in Dominy (2016), Lyman, Robertson & Day (2016), Dominy et al., (2018), Esbensen (2020), Esbensen et al., (2021) and Pitard (2019).

Where an existing project is looking to switch to PhotonAssay™, it can undertake a feasibility evaluation on applicability. At this stage, it is key for the CP/QP to have a clear understanding of the mineralisation in question and what the sampling and analysis requirements are.

A generic comparison protocol between existing assay results and PhotonAssay™ may look like:

- Select more than 150 coarse sample rejects whose original assay grade represent the grade distribution for a given domain;
- For each reject, crush to P₈₀ 2 mm (if required) and riffle split two equal 350-500 g portions, each to be placed in a PhotonAssay[™] jar. PhotonAssay[™] the two jars.
- Recombine both jars and pulverise to P₈₀ 75 µm and riffle split two equal 350-500 g portions, each to be placed in a PhotonAssay™ jar. PhotonAssay™ the two jars.
- From each jar of pulverised material, FA each to extinction or least riffle split off two to four 30 g sub-samples. SFA or LW/PAL of each jar may be appropriate if coarse gold is suspected.

This protocol provides several conciliation points between the original assay, crushed material by PhotonAssay™, pulverised material by PhotonAssay™, effects of averaging two jars and a final direct comparison to FA (or SFA). The cost and environmental considerations must also be part of any feasibility study.

The alternative to undertaking a feasibility study is to design an optimised protocol using PhotonAssay™ and implement this across either an in-fill drilling programme or carefully re-sample and assay previous sample rejects.

Alternative assay methods for comparison can be embedded into the protocol. Such work needs to be designed and expedited by the CP/QP and is not simply a statistical process. A "smart" data-collaborative approach to optimisation is preferred that includes understanding the mineralisation and its sampling needs (Dominy, Xie & Platten, 2008; Dominy, et al., 2021; Dominy, Glass & Purevgerel, 2022; Pitard, 2015; Villanova, Heberle & Chieregati, 2017). Case studies 1 and 2 highlight this approach.

2.3.2 The Need for QAQC

For all assay programmes, QAQC are non-negotiable (Simon & Gosson, 2008). In practical terms, QC procedures monitor precision and accuracy of data, as well as sample contamination during preparation and assaying (Simon & Gosson, 2008). Resource and grade control drilling and assaying programmes will have a QAQC component, where the main considerations are:

- Duplicate field, laboratory and analytical samples.
- · Insertion of CRMs and analytical blanks.
- · Insertion of process blanks.
- · Monitoring of sample crush and split quality.
- · Submission of samples for umpire assay.
- Written and audited laboratory procedures with appropriate staff supervision to ensure compliance.
- Regular audits of the laboratory by the CP/QP.

Samples must be submitted for umpire assay by PhotonAssay[™] followed by another method such as SFA or LW (with tails assay). All umpire work should be undertaken at a separate independent laboratory to the principal laboratory.

2.3.3 Certified Reference Materials

CRMs are used for both company QC purposes and by the laboratory operator/Chrysos for unit calibration and internal monitoring (Chrysos, 2023a).

PhotonAssay™ specific CRMs are now available, with the first being released by OREAS during 2021. Subsequently, in June 2023 fifteen of the CRMs were issued new certification in which both the certified grade and SD had changed. OREAS noted that it had "embarked upon a significant 'Au by PhotonAssay™' recertification programme for 15 OREAS CRMs. This programme was specifically tailored to address some bias features discovered late last year [2022] in the original PhotonAssay™ certification.

This recertification programme is much more extensive than what was possible initially" (OREAS, 2023a). The recertification resulted in grade changes across the 15 CRMs of between -0.8% and +5.1% relative to the previous grade (OREAS, 2023b). The quantum of changes is within reasonable expectation of the SD delta for each when considered relative to the mean grade change. The variations in grade changes between the old and new CRMs are not statistically significant. Combining the 1SD uncertainties from the old and new certifications provides the total uncertainty on the grade change. There is an overall 2.9% change in average grade (note this value is based on all 15 OREAS CRMs, covering a grade range of 0.31 g/t Au to 43.24 g/t Au). CP/QPs are cautioned to review the results of any programme using OREAS CRMs, particularly across the time period of both sets of certifications.

Historically, PhotonAssay™ units have been calibrated against commercial CRMs, typically adopting the certified FA grades. This approach was followed as FA grades were considered to be the best estimates of the true gold content (compared to other existing analytical methods) and to ensure continuity with clients' earlier data sets obtained using FA. More PhotonAssay™ machines are now available for CRM round-robin evaluations, together with 'first-principles' materials prepared from high-purity gold and a blank substrate (e.g. "k-cal" process, see Section 2.1.3). This has led to some systematic deviations in FA grades becoming apparent, with a number of CRMs underreporting gold via FA by 2-3% compared to PhotonAssay™. This difference is attributed to a combination of: (a) the quoted FA grade uncertainty; (b) statistical uncertainty on the mean estimated PhotonAssay™ grade; (c) small systematic differences between the two methods e.g. lower FA recovery in refractory materials; and (d) small systematic differences between FA certification process followed by different manufacturers e.g. selection of laboratories, handling of outliers, etc.

The most effective calibration and monitoring comes from using materials with accurately certified PhotonAssay™ grades to generate consistent results. Mixing-and-matching FA and PhotonAssay™ certified grades can lead to issues, especially if by chance the selection of materials happens to show a mostly one-sided FA versus PhotonAssay™ difference.

The CP/QP should consult with the laboratory to agree on the use of CRMs for internal laboratory monitoring purposes. These CRMs should be inserted into client batches along with the client CRMs.

Chrysos recommend a monitoring CRM insertion rate of 5% (1 in 20), where CRMs should, as noted above be certified for PhotonAssay™ and cover a grade range of >0.3 g/t Au up to 80 g/t Au (Chrysos, 2022b, 2023).

It is important to ensure that PhotonAssay[™] jars are filled above 50% or they will be rejected. A fill of >80% is optimal. Over time, settlement may occur within jars, particularly where pre-filled CRM jars are re-used. It has been noted that differences in fill proportion can lead to progressively biased results with time. This relates to situations where the CRM pulp fill settles with time but reports a high fill factor due to a "dusting" of fine pulp at the top of the jar thus recording the high fill factor when it may be low, even <50%. Also, it should be noted that when a CRM is first put through the PhotonAssay™ unit its mass and fill factor are recorded - these values are re-used each time the CRM is run and not determined on each use. Therefore if a CRM is used for six months, then its mass/fill value on first use is applied over the six months. It is therefore critical that CRM jars must be fully filled and their contents well packed in line with recommendations from Chrysos (2020; 2022b). Their fill levels and masses should be monitored on a weekly basis. Full re-jarring should be undertaken every four weeks. In any case, re-jarring should occur after c. 65 uses (assuming the standard two-cycle assay: PAAUo2) as the X-rays lead to a deterioration of the plastic jar. Potential effects on the CRM with time are: loss of CRM material by leakage, damage or handling, and/or effects of moisture and/or oxidation.

2.3.4 Disposal and Recycling of Jars

The storage and disposal of sample material is a key consideration for the CP/QP, who needs to consider the need for retention or not. In general, samples informing a new pre-operational project or resource development project should be retained. Samples related to grade control can more likely be disposed of. Given that PhotonAssay™ is non-destructive, analysed samples can be recombined for metallurgical or other testwork (Arrowsmith, Parker & Dominy, 2019; Dominy et al., 2023).

PhotonAssay™ jars and lids are made from polyethylene and so are suitable for recycling. Some groups are currently investigating the utility of robotic facilities to unscrew jar lids and clean them for re-use.

An average jar weighs 34 g, so a big assay programme could reach >1M jars comprising >34 tonnes of plastic, a factor to consider if samples are disposed to landfill.

Such a programme could also yield >400 t of jarred sample material. Various groups are trialing options for the re-use and/or recycling of PhotonAssay™ jars.

2.3.5 Positional Heterogeneity in Jars in the Presence of Coarse Gold

Samples containing coarse gold may display a positional heterogeneity when using PhotonAssay™. When a sample jar bearing coarse gold is presented to the PhotonAssay unit, a grade is determined based on the geometry between the coarse gold particle(s) within the jar, the detectors and X-ray source. If the jar contents are subsequently disturbed by movement (e.g. transport of the jar), then the relative location of gold particles may have moved, thus potentially providing a different grade on re-assay.

During a testwork programme undertaken on coarse gold mineralisation, 50 jars were assayed then "shaken" for 30 seconds and re-assayed. The re-assays displayed a bias of -3.9% between the original and re-assay grades, with a pairwise precision of $\pm 19\%$.

The uncertainty estimated on the bias was 4.6%, which shows that the bias is not significant (<2SD). The heterogeneity effect increases the total measurement error (sampling and instrument) by a factor of c. 2% compared to the sampling only error (i.e. pretty much negligible). And if the sampling error is estimated empirically by comparing results for different aliquots drawn from the bulk lot, then this additional 2% contribution is already included.

With the style of mineralisation tested, higher variability was seen above 0.5 g/t Au, which is in accordance with other testwork that indicates coarse gold >250 μ m at this grade and above and up to a few mm in size (Dominy & Graham, 2020; Dominy, van Roij & Graham, 2022).

This effect is only likely to affect coarse gold dominated mineralisation where a single dominant gold particle or unbroken gold cluster is present. It is highly unlikely to occur with every jar. In this case, ten PhotonAssay™ jars were averaged to yield a grade (Dominy & Graham, 2020). In the fine gold mineralisation example, the authors are aware of a similar experiment, which resulted in low bias (<0.5%) and high precision (<5%) values.

2.3.6 Assay Cost

The cost of PhotonAssay[™] and associated sample preparation is dependent upon geographical location, laboratory, protocol applied and contract conditions with

the given laboratory. Based on analysis of selected "book prices" from Australian laboratories, the cost of PhotonAssay™ and other assays, with FA as the common denominator are presented. PhotonAssay™ (PA 500 g) yields 1.03x cost units (e.g. the same as FA), LeachWELL (LW 1000 g) 1.45x cost units, and screen fire assay (SFA 1000 g) 3.25x costs units. The reader is cautioned however, that this is a simple comparison that does not reflect contract-by-contract arrangements.

2.4 The Importance of "Rig-to-Assay" Optimisation

2.4.1 Fundamental Sampling Error evaluation

The FSE is dependent upon the Constitution Heterogeneity, which relates to sample weight, mineral fragment size and shape, liberation stage of the gold, gold grade, and gold and gangue density. It is the smallest residual sampling error that can be achieved even after homogenisation of a lot or a sample lot been carried to fulfilment, i.e. the material is in its intrinsic minimum residual heterogeneity state. When FSE is not optimised for each sub-sampling stage, it often becomes a major component of the sampling nugget variance (Francois-Bongarcon, 2004; Pitard, 2007, 2019; Dominy, 2014; Esbensen, 2020).

The FSE can be theoretically estimated before a lot of material is sampled, provided the sampling characteristics (e.g. the sampling constant - K) embedded in the FSE equation are determined (Gy, 1982; Pitard, 2019). The "FSE equation" can be used to optimise sampling protocols (Gy, 1982; Pitard, 2019), where it addresses key questions of sampling broken rock:

- What weight of sample should be extracted from a larger mass of mineralisation, so that the FSE will not exceed a specified variance?
- What is the possible FSE when a sample of a given weight is obtained from a larger lot?
- Before a sample of given weight is drawn from a larger lot, what is the degree of crushing or grinding required to lower error to a specified FSE?

Pitard (2013) states that the total allotted sampling error (TSE) for resource grade sampling should be less than $\pm 32\%$. The component FSE should not exceed c. $\pm 19-21\%$ (over two to three sample reduction stages). Whilst a target FSE of less than $\pm 21\%$ is reasonable, it may be hard to achieve in the presence of coarse gold. A FSE target of $\pm 30\%$ may be more realistic.

In practice, the TSE may in general vary between $\pm 20-90\%$, with typical components of field sampling ($\pm 20-90\%$), sample preparation ($\pm 5-40\%$) and analysis ($\pm 1-25\%$) (Stanley & Smee, 2007; Dominy, Purevgerel & Esbensen, 2020).

The use of the FSE equation represents a model approach that may, or may not, be a fully relevant match with geological reality, but which at least provides a starting point from where protocols can begin to be compared and optimised (Gy, 1982; Pitard, 2019). Reliable use of the FSE equation is critically dependent on that all ISE (and GSE) have been optimally eliminated or reduced (Pitard, 2019; Esbensen, 2020). Results of QC programmes will provide evidence for precision optimisation (repeatability) through application of field and laboratory duplicates (Stanley & Lawrie, 2007; Stanley & Smee, 2007; Abzalov, 2008; Carswell et al., 2009; Dominy, Purevgerel & Esbensen, 2020). Sampling accuracy is dependent on the application of TOS ISE management rules along the complete lot-to-aliquot pathway (Esbensen, 2020). Further discussion and presentation of the FSE equation is provided in Gy (1982), François-Bongarçon (1998), François-Bongarçon & Gy (2002) and Pitard (2019). In the present contribution, the François-Bongarçon (1998) modified FSE equation is applied.

3. Case Studies

3.1 Case Study 1: Examples of FSE estimation for the worst case scenario

3.1.1 Introduction

An example is presented from an open pit operation, which is a well-characterised lode gold deposit with two distinct domains of sulphide mineralisation. One domain is dominated by <75 μ m gold (D1), whereas the other is dominated by coarse gold >200 μ m (D2). D1 sits on the footwall of D2, and is characterised by shearing, disseminated sulphides and minor quartz veining 10–15 m in width. D2 is a high grade (4–5 g/t Au) high-density quartz veining zone 5–10 m in width.

RC and diamond core drilling are used for resource development and grade control drilling. RC drilling accounts for c. 80% of all drilling on the site. Metallurgical and mineralogical sampling and testwork programmes have characterised the mineralisation in both domains, in particular, the nature of the gold particle size distribution. The D1 mineralisation has a sampling constant (K) of c. 5-150 g/cm, whereas the D2 mineralisation K range is 400-4,500 g/cm. The high D2 value is driven by the coarse nature of the gold (>100 μm to 500 μm).

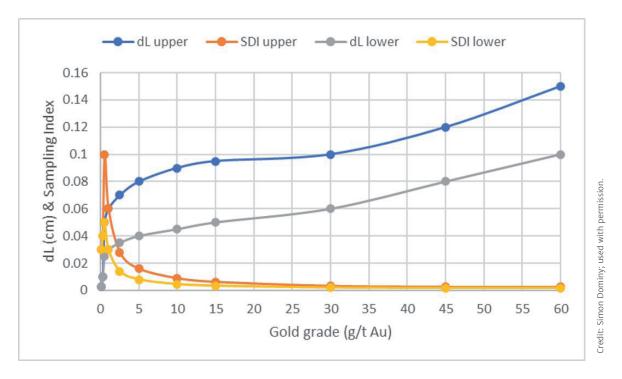


Fig. 4: Plot showing the relationship between gold grade and upper/lower gold particle sizing $(d\ell)$ for D2 mineralisation with the sampling difficulty index.

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Figure 4 shows the relationship between gold grade and gold particle sizing in the D2 mineralisation (d ℓ - liberation diameter: Pitard, 2019; Dominy et al., 2021). This is based on testwork, where the relationship presented shows the general trend of the data. The upper and lower d ℓ values are shown for the given grade. The sampling difficulty index, i.e. ratio of d ℓ with grade is defined such that any value >0.05 may indicate sampling challenges. In this case, a grade of 0.5 g/t Au displays the worst case scenario.

The FSE calculations presented below are based on the mining (open pit) breakeven cut-off grade of 0.5 g/t Au, also given as the worst case scenario. Table 4 shows the original sampling protocol applied for each domain, with FSE analysis for D2 mineralisation.

FSE for the D1 mineralisation based on a 30 g FA, works well with an FSE of less than ±15%.

For D2, the protocol is poor with a calculated total FSE range of greater than $\pm 30\%$ and up to $\pm 102\%$. For the D1 protocol, the largest proportion of FSE relates to the pulp split, whereas the rig split becomes dominant in the D2 protocol.

The reader is reminded that the errors calculated here are solely the FSE, and no account is made for GSE, DE, EE or PE.

A revised protocol was subsequently recommended using PhotonAssay™ (Table 5).

For the revised protocol, the D1 protocol is acceptable with no change in the FSE. However, in the D2 protocol there is a worsening of the total FSE related to the splitting of 500 g for PhotonAssayTM from the 3 kg rig split. This is driven by the coarse nominal fragment (dN = 4.5 mm) and gold particle size (d ℓ = 500 um). The rig split is the same (3 kg from 35 kg). For the worst case, a rig split of c. 24 kg is required, followed by a lab split of 13 kg to achieve a \pm 30% FSE (Figure 5).

The entire 13 kg could be assayed via PhotonAssay™ or crushed to c. 1 mm and 6.5 kg assayed maintaining an FSE of ±30%.

Figure 6 shows the rig and lab mass splits required across the grade-d ℓ values previously noted. The highest mass requirements correlate with lower grades and the high sampling difficulty indices (Figure 4).

Tab. 4: Original sampling protocols applied for D2 with resulting FSE based on the low and worst case scenarios.

Protocol		Lov	v case	Worst case	
Stage	Step	FSE	Rel. prop.	FSE	Rel. prop.
RC rig split	35 – 3 kg	±24%	49%	±79%	60%
Lab crush	3 – 1.5 kg	±19%	30%	±55%	30%
Pulverise & assay	1.5 kg – 30 g	±16%	22%	±32%	10%
Total	-	±34%	100%	±102%	100%

Rig split at P_{00} 4.5 mm; laboratory splits at P_{00} 3 mm; assay split as P_{00} 75 μ m. Low case $d\ell$ = 150 μ m and worst case $d\ell$ = 500 μ m.

Tab. 5: Revised sampling protocols applied for D2 mineralisation, with resulting FSE based on the low to worst case scenarios.

Protocol		Lov	Low case		Worst case	
Stage	Step	FSE	Rel. prop.	FSE	Rel. prop.	
RC rig split	35-3 kg	±24%	25%	±79%	29%	
Lab crush & assay	3-500 g	±42%	75%	±124%	71%	
Total	-	±48%	100%	±147%	100%	

Rig split at P_{90} 4.5 mm; laboratory splits at P_{90} 3 mm. Low case $d\ell$ = 150 μ m and worst case $d\ell$ = 500 μ m.

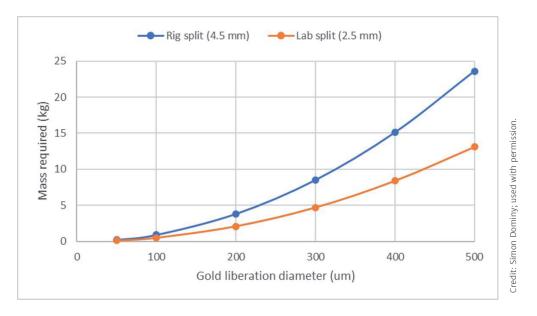


Fig. 5: Plot of mass required for the rig and laboratory splits at a grade of 0.5 g.t Au for various gold liberation diameters.

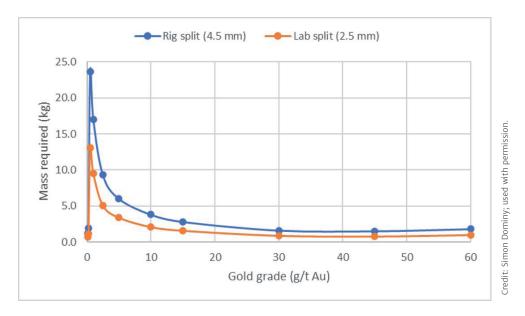


Fig. 6: Plot of mass required for the rig and laboratory splits at a series of grades based on the worst case gold grade-dℓ relationship presented in Figure 4.

Tab. 6: Revised sampling protocol applied to D2 mineralisation, with resulting FSE..

Proto	Protocol Low case		Worst case		
Stage	Step	FSE	Rel. prop.	FSE	Rel. prop.
RC rig split	35 – 10 kg	±12%	30%	±24%	25%
Lab crush & assay	10 – 2.5 kg	±18%	70%	±42%	75%
Total	-	±21%	100%	±69%	100%

Rig split at P $_{90}$ 4.5 mm; laboratory splits at P $_{90}$ 3 mm. Low case d ℓ = 150 μ m and worst case d ℓ = 500 μ m.

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The problematic grades lie between 0.3 g/t Au and 1.4 g/t Au, which includes the breakeven cut-off grade of 0.5 g/t Au.

A decision was made for further optimisation, specifically to take a 10 kg rig split followed by 2.5 kg at the laboratory for assay (Table 6). As before, the intention was to use PhotonAssay™, but the option exists to pulverise the entire 2.5 kg and assay via LeachWELL.

In this case, the calculated FSE for the worst case is high, though for the low case is acceptable.

3.1.2 Stage-wise error evaluation

Errors representing the repeatability of assay results can be estimated by pairwise analysis of field, coarse and pulp duplicates (Stanley & Lawrie, 2007; Abzalov, 2008; Carswell et al., 2009; Dominy, Purevgerel & Esbensen, 2020). Sampling protocols include several stages of comminution and subsampling, where duplicates can be taken at every stage to allow estimation of the total sampling precision error and the relative contributions at the different stages of the sampling protocol (e.g. sampling, preparation and analysis error).

Stanley & Lawrie (2007) and Abzalov (2008) have shown that the coefficient of variation, or the Relative Sampling Variability (RSV) estimated from paired data produces a reasonable estimate of sampling precision.

Component errors reflect the ore type, sample type and collection and proceeding preparation and analysis. Total sampling error (as RSV) is likely to be in the range $\pm 25-100\%$ for gold ores, with components of $\pm 20-90\%$ (sampling), $\pm 5-40\%$ (preparation) and $\pm 1-25\%$ (analytical) respectively.

Throughout this contribution, the relative sampling precision from duplicate pairs is calculated via the RSV at 1SD (68% reliability). All data is filtered at the 10x detection limit. All duplicates were collected as cascading pairs from the same field sample. Table 7 shows analysis for the original protocol.

The dominant error relates to the rig split, followed by the laboratory and pulp splits. The pulp split is high due to the presence of coarse gold related to delayed comminution. The reader is reminded that the duplicate errors include all errors: FSE, GSE, DE, EE, PE and AE. Table 8 shows analysis for the revised protocol (Table 6) based on the application of PhotonAssay™.

It should be noted that number of duplicates is low due to the recent introduction of PhotonAssay™. This data set displays a marked improvement from the original protocol. The total error, field/rig split is reduced from ±75% to ±52%.

For PhotonAssay™, the analytical RSV is provided as the jar or groups of jars can simply be re-assayed.

Tab. 7: Global pairwise precision estimate for the original D2 mineralisation protocol. Error provided as relative sampling variance (RSV).

	Field/ RC rig split RSV	Lab split RSV	Pulp RSV
Duplicate RSV	±75%	±49%	±26%
Stage RSV	±55%	±42%	±26%
Relative proportion	56%	32%	12%
Number of duplicates	350	350	350

Tab. 8: Global pairwise precision estimate for the revised D2 mineralisation protocol. Error provided as relative sampling variance (RSV).

	Field/RC rig split RSV	Lab split RSV	Analytical RSV
Duplicate RSV	±52%	±40%	±7%
Stage RSV	±33%	±39%	±7%
Relative proportion	51%	57%	2%
Number of duplicates	120	120	120

No splitting is required. In this case, an analytical RSV of $\pm 7\%$ is acceptable.

3.1.3 Case 1 - Conclusions

Testwork during a Mineral Resource update displayed on improvement in the total nugget effect based on comparison between an area containing 300 holes of the original RC-FA, which was infilled with 125 holes assayed via the revised RC-PhotonAssay™ protocol. The original modelled nugget effect was 70% versus a reduced value of 50% which indicates the new PhotonAssay™ protocol is working. No change in geology or grade continuity was noted, suggesting that the reduction in total nugget relates to the SNE.

3.2 Case Study 2: Change from Fire Assay to PhotonAssay™ in a fine gold mineralisation

3.2.1 Introduction

In a second case study, a small shear-zone style open pit deposit contains minimal coarse gold. Drilling was by RC, originally using FA and then testing with PhotonAssay $^{\text{TM}}$.

For both programmes, the RC drilling produced c. 30 kg 1 m composites from which 3–4 kg were split at the rig. For the initial programme, the total rig sample was crushed at the laboratory to P_{80} 2 mm and 1 kg split for pulverisation.

A 30 g charge was taken for FA. For the subsequent programme, the total rig sample was crushed at the laboratory to P_{80} 2 mm and 500 g RSD split for a single PhotonAssayTM assay.

Table 9 shows the global pairwise precision estimate for the FA protocol. Table 10 shows the global pairwise precision estimate for the PhotonAssay™ protocol.

It can be seen from Table 9 and 10, that the dominant error (Stage RSV) in the protocols is the field/rig split at $\pm 34\%$ and $\pm 32\%$ absolute. As a relative proportion of the entire protocol these are 92% and 80% respectively.

There is some difference between the lab/coarse splits of $\pm 9\%$ to $\pm 16\%$, which relates to the lab/coarse split changing from 3 kg to 1 kg (original) to 3 kg to 0.5 kg (revised). As a relative proportion of the entire protocol these are 6% and 19% respectively.

In the initial protocol, the pulp split yields a precision of $\pm 5\%$ compared to the subsequent protocol of $\pm 2\%$. In the initial protocol, the precision includes both splitting and analytical errors. For the subsequent protocol, it represents the repeat assay of the same jar, effectively the analytical error.

Tab. 9: Global pairwise precision estimate for a low-coarse gold mineralisation via FA protocol. Error provided as relative sampling variance (RSV).

	Field/RC rig split RSV	Lab/coarse split RSV	Pulp RSV
Duplicate RSV	±35%	±10%	±5%
Stage RSV	±34%	±9%	±5%
Relative proportion	92%	6%	2%
Number of duplicates	240	240	240

Tab. 10: Global pairwise precision estimate for a low-coarse gold mineralisation via PhotonAssay™ protocol. Error provided as relative sampling variance (RSV).

	Field/RC rig split RSV	Lab/coarse split RSV	Analytical RSV
Duplicate RSV	±36%	±16%	±2%
Stage RSV	±32%	±16%	±2%
Relative proportion	80%	19%	<1%
Number of duplicates	125	125	125

3.2.2 Case 2 - Conclusions

This case study indicates that the switch to PhotonAssay™ in this instance did not add great advantage, based on precision of the sampling protocol. Testwork during a Mineral Resource update indicated no change to the nugget effect (c. 20%) based on comparison between areas of RC-FA and RC-PhotonAssay™.

In general, there are no barriers to the application of PhotonAssay[™], other than high levels of interfering elements (e.g. U-Th, Ba and Pb). Additional advantages include reduced CO₂, safer − no lead or cyanide used, and elimination of mix-ups and/or errors in the FA or analytical laboratory.

3.3 Case Study 3: Evaluation of different postcoarse crush splitting methods

3.3.1 Introduction

A key action in any protocol is the post-crush (coarse) laboratory split before assay. This is particularly important when using PhotonAssayTM, as this is the split that feeds the PhotonAssayTM jars for direct assay. The general recommendation is that PhotonAssayTM uses a split of P_{80} to P_{90} 2 mm, though pulverisation is not precluded if appropriate.

Based on a moderately coarse gold mineralisation, testwork was undertaken to investigate the splitting of a 2.5 kg (5x PhotonAssay™ jars) composite assay charge.

Seventy-five 10 kg RC field samples were chosen based on their original assay value to ensure a representative range of grades greater than ten times the detection limit (>0.5 g/t Au).

The primary protocol was based on the crushing of 10 kg samples to P_{8o} 2 mm and RSD splitting of 2.5 kg from each. This 2.5 kg was placed in five PhotonAssayTM jars and assayed. From the selected retained residues, a further 2.5 kg sub-samples were split to from 75 RSD split pairs. The duplicate 2.5 kg splits were placed in five PhotonAssayTM jars and assayed.

Post assay, the two sets of 2.5 kg RSD splits were combined back with the 5 kg residue to from the "original" 10 kg sample.

These were poured in their entirety into a large tray, where two 2.5 kg splits were scooped from the 10 kg lot, placed in PhotonAssay™ jars and assayed. The scooping process can be likened to grab sampling along with its inherent errors (Gy, 1982; Dominy, 2010; Esbensen & Wagner, 2017; Pitard, 2019; Esbensen, 2020; Minnitt, 2022).

Table 11 shows the global pairwise precision for the original 2.5 kg PhotonAssayTM charge via RSD. The lab/coarse split stage RSV component is $\pm 34\%$, representing 34% of the total protocol error.

Tab. 11: Global pairwise precision estimate for the original 2.5 kg PhotonAssay[™] charge via RSD splitting. Error provided as relative sampling variance (RSV).

	Field/rig split RSV	Lab/coarse split RSV	Pulp RSV
Duplicate RSV	±59%	±35%	±7%
Stage RSV	±47%	±34%	±7%
Relative proportion	65%	34%	1%
Number of duplicates	75	75	75

Tab. 12: Global pairwise precision estimate for the second 2.5 kg PhotonAssay[™] charge via scooping. Error provided as relative sampling variance (RSV).

	Field/rig split RSV	Lab/coarse split RSV	Analytical RSV
Duplicate RSV	±67%	±47%	±7%
Stage RSV	±47%	±46%	±7%
Relative proportion	50%	49%	1%
Number of duplicates	75	75	75

Table 12 shows the global pairwise precision for the repeat 2.5 kg PhotonAssayTM charge via scooping. The lab/coarse split RSV component is now $\pm 46\%$, representing 49% of the total protocol error. The scooping split has increased the overall RSV from $\pm 59\%$ to $\pm 67\%$.

The scooping operation has increased the error focus onto the lab/coarse split stage, compared to using the RSD where the key error was associated with the rig split. The change from RSD to scooping effectively increases the stage RSV from $\pm 34\%$ to $\pm 43\%$ for the lab/coarse split process.

This increased error relates to the presence of coarse gold in the -2 mm fraction, with gold particles up to 500 μ m in size observed. Eight of the 75 2.5 kg assay charge samples with grades >0.5 g/t Au were panned to check for visible gold, with both gold in rock particles and minor free gold observed.

3.3.2 Case 3 - Conclusions

This case study shows clearly that the laboratory/coarse sample split must be undertaken correctly to minimise sampling errors. The original protocol where the rig/field error dominates, swaps in the second protocol due to the dominant laboratory/coarse split error due to scooping. Note the limitation of this study is that only 75 sample pairs were used, that being a practical number given the effort involved.

The general paradigm for PhotonAssay™ is to crush to P₈₀₋₉₀ 2-3 mm and split into the relevant number of jars. This split size and mass must be optimised to reduce the FSE and the correct splitter used to minimise bias. Riffle or RSD type splitters are appropriate as either bench top or automated (e.g. Boyd or Orbis crushers and associated splitters) units (Petersen, Dahl & Esbensen, 2004; Esbensen & Wagner, 2017; Pitard, 2019; Esbensen, 2020). Like any piece of sampling equipment, an RSD or riffle splitter must be set up properly and operated correctly. Any kind of scooping or grabbing is likely to lead to enhanced bias. Crush quality and split precision must be monitored as part of the QC process.

Arguments against the laboratory use of an RSD usually focus on greater time and higher cost requirements. The CP/QP needs to weigh up the pros and cons. A riffle splitter is an effective, quicker and cheaper option.

3.4 Case Study 4: Calibration of gold ores

3.4.1 Background

In the context of broken rock, the FSE is the smallest residual error that can be achieved even after homogenisation of a sample lot is attempted (Gy, 1982; Pitard, 2019). The FSE is dependent upon the constitution heterogeneity, which relates to sample weight, mineral fragment size and shape, liberation stage of the gold, gold grade, and gold and gangue density. The FSE can be estimated before the material is sampled, provided the sampling characteristics (e.g. K and α) embedded in the FSE are determined. Heterogeneity tests lead to the calibration of K and α and back-calculation of the liberation diameter - dℓ (Minnitt, Rice & Spangenberg, 2007; Minnitt & Assibey-Bonsu, 2009; Pitard, 2015; Minnitt, Francois-Bongarçon & Pitard, 2017; Villanova, Heberle & Chieregati, 2017; Dominy et al., 2021; Chieregati et al., 2023). dℓ can be equated to dAu95 - effectively the screen size that retains 5% of gold given a theoretical lot of liberated gold. Where gold particles cluster, the $d\ell$ becomes $d\ell$ clus, which is the equivalent spherical diameter (ESD), or the composite particle formed by the cluster group (Dominy & Platten, 2007).

There are several different types of heterogeneity test, which in the simplest sense are the standard Heterogeneity Test (HT; Gy, 1982) and the Duplicate Series Analysis (DSA; Minnitt, Rice & Spangenberg, 2007) and variants. The key outputs of such test are the sampling constant (K) and so-called alpha (α). The standard heterogeneity test attempts to isolate the FSE, whereas the DSA estimates the first component of the quality fluctuation error (QFE1), i.e., the FSE plus the grouping and segregation error (GSE). Debates have taken place addressing the limitations of the various approaches and the true nature of variability measured in heterogeneity experiments. To date, there is no agreement on which approach is correct. However, for heterogeneous mineralisation such as gold, a more integrated approach using various inputs (e.g. metallurgical testwork, mineralogy/mineral deportment and field observations) may be appropriate (Pitard, 2015; Villanova, Heberle & Chieregati, 2017; Dominy et al., 2021; Chieregati et al., 2023).

PhotonAssay™ provides an excellent methodology for the analysis of material for heterogeneity testwork (Tremblay, Wheeler & Oteri, 2019). Its non-destructive nature allows for additional verification work through metallurgical and/or X-ray tomographic approaches. Some preliminary studies are reported below.

3.4.2 Calibration by DSA

A DSA calibration approach was used on a mineralisation type known to contain coarse gold. The mineralisation is characterised by quartz-sulphide veins with free gold associated with the sulphides, with an underground run-of-mine grade in the 14-16 g/t Au range. Based on knowledge at the time, it was estimated that 350 kg was required to be collected from the plant feed belt (P_{80} 80 mm) to achieve $\pm 20\%$ FSE at the 1SD confidence limits. A primary lot of run-of-mine was collected as a series of increments from the plant feed belt over a single process shift of 12 hours (c. 400 tonnes of ore feed). The increments were collected by stopping the belt 24 times over the 12 hour period, effectively at random within each 30 minute period. Each 15.5 kg increment was manually cleared from the belt.

The DSA methodology and associated outputs of Minnitt, Rice & Spangenberg (2007) were followed. The global value for K was 225 g with an α value of 1.3. The back-estimated d ℓ value was 110 μ m. The K and d ℓ values were estimated for each size fraction based on the work of Lyman (2019; 2023).

Assuming traditional values of 0.25 for the granulo-metric factor and 0.5 for the shape factor (sphere), the effective top size of the particles/clusters can be backestimated (Lyman, 2019; 2023). The results are given Table 13.

In the coarsest fraction [1], the gold particles cluster to 750 μ m, though as comminution progresses the particle reduces to 125 μ m.

Figure 7 shows the reduction in effective gold size with nominal particle size.

The recognition of gold clusters is consistent with core logging and underground mapping, where composite clusters (including quartz-sulphide material between individual gold particles) of a few mm to 2 cm are observed. Clustering is material to any part of the sampling process where they exist, from in-situ rock to crushed material (Dominy & Platten, 2007; Dominy et al., 2021; Dominy, Glass & Purevgerel, 2022).

Tab. 13: Calculated values of K and $d\ell$ for gold mineralisation using PhotonAssayTM.

Series	1	2	3	4
dN nominal size (mm)	25	3	1	0.5
K (g)	65	2	1	0.6
dℓ/dℓclus (μm)	750	225	190	125

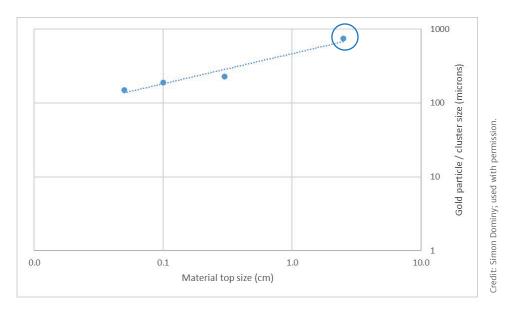


Fig. 7: Estimated size of gold clusters as a function of sample nominal size. The cluster size within 2.5 cm sized material is 750 μ m.

3.4.3 Direct calibration via testwork and X-ray computed tomography

As part of a validation study presented in the previous section, PhotonAssay[™] jar contents were subjected to X-ray computed tomography (XCT) to resolve gold particle size (Howard et al., 2011; Dominy et al., 2012; Kyle & Ketcham, 2015; Dominy et al., 2021). Samples were scanned as a series of lots, with the final gold particle size data combined for analysis. The effective resolution of the XCT was 50 μm.

Following the XCT study, each set of jars were recombined as one sample and subjected to a crush-liberation-gravity (CLG) concentration process. At each of three stages, the gold was concentrated via Mosely Table and/or spiral panner and the gold particle sizes measured. Table 14 reports the DSA (Sample #7 only), CLG and XCT results compared to the core logging (GEO).

Tab. 14: Results for samples assayed by PhotonAssay[™], scanned by XCT and processed via CLG.

[--] values represent composite gold particle size of cluster. Non [--] values represent single particle size.

All particle sizes as ESD.

Sample No.	PhotonAssay™ bulk grade (g/t Au)	Nominal max. particle size (mm)	Total mass (kg)	DSA d <i>l</i> (μm)	CLG dℓ (μm)	XCT dℓ (μm)	GEO d <i>l</i> (μm)
1	0.5	5	5	-	70	_	-
2	1.7	5	5	-	100	150	-
3	3.2	5	5	-	135	-	-
4	5.5	5	5	-	160	[550]	[400]
5	8.4	5	5	-	125	[600]	[700]
6	10.6	5	5	-	470	[350]	[1,250]
7	15.2	5	5	110 [750]	350	[1,050]	[1,650]
8	26.5	5	5	-	540	[1,350]	[1,800]

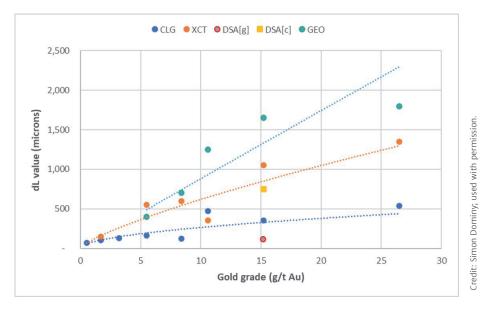


Fig. 8: Gold particle size data from the DSA, CGL and XCT analysis. GEO: Geological logging of core; CLG: Crush-liberate-gravity; XCT: X-ray computed tomography; DSA: Duplicate series analysis, [g] global dℓ and [c] clustered dℓ.

The particle size data from Table 14 is presented in Figure 8.

The CLG data provide a non-clustered $\mathrm{d}\ell$, given that the gold is liberated, and clusters destroyed. The XCT data was scanned at a 2.5 cm nominal size and has thus resolved any clustering present at that scale. The cluster values presented represent a single particle composited from the cluster group. The value from geological logging of core (GEO) is a generic observation of clusters from core intersections of the same grade as the samples — it is not from the actual samples.

The DSA results for sample #7 represent a mathematical manipulation of assays rather than a direct measurement of gold particles. The approach has identified the possibility of clustering (d ℓ = 750 µm) which is confirmed by geological observation (d ℓ = 1,460 µm) and XCT scanning (d ℓ = 1,050 µm). Whilst the d ℓ values are different, the XCT represents a scanned sub-set of the original DSA lot (5 kg versus 15 kg), and the geological observation is not from the same lot but from the same mineralisation.

The definition of $\mathrm{d}\ell$ versus $\mathrm{d}\ell_{\mathrm{clus}}$ is a different proposition across available methodologies. The DSA is an averaging process that is dependent upon the representativity of the original sample lot. The largest cluster values relate to geological logging of core which are more representative over 1,000's m of core but may be biased high as the measurement of the composite particle ESD is based on human interaction with the core, e.g. hand lens and ruler and stereographic effects (e.g. 2D observation of the core surface).

The best evaluation of clusters comes from XCT, given that a direct measurement is taken and that the composite size can be better evaluated in 3D (Dominy et al., 2021). Though like all methods, XCT also has its limitations in particular interferences between gold particles (e.g. star and streak effects: Howard et al., 2011; Kyle & Ketcham, 2015).

3.4.4 Case 4 - Conclusions

The calibration data in Case 4 emphasises the need to crush drill core to 2 mm to minimise the effect of clustering on subsequent splitting.

A post-testwork analysis shows that the selected 350 kg DSA primary sample mass was reasonable, yielding an FSE of $\pm 19\%$ based on a d ℓ clus of 750 μ m, grade of 14 g/t Au and α of 1.3. If the highest d ℓ clus value of 1,650 μ m (from GEO, Table 13) is applied, then the FSE rises to $\pm 36\%$. A major challenge with calibration tests such

as the DSA, is the representativity of the sample mass selected.

In coarse gold environments assumed masses may be unrepresentative, placing doubt on test results (Pitard, 2015; Villanova, Heberle & Chieregati, 2017; Dominy et al., 2021; Chieregati et al., 2023). In this case, the high grade of the ROM plant feed reduced the mass required.

If the mine cut-off grade (3.5 g/t Au) was targeted, then the required mass is likely in the range of 0.5–1 t. This raises the question as to the most appropriate grade to optimise to. Given the importance of the mine cut-off grade, this should perhaps be the target for calibration (Dominy & Xie, 2016; Dominy, Glass & Purevgerel, 2022).

Where possible, *a priori* data should be used during planning to investigate the representative sample mass required and post-calibration for validation of results (Pitard, 2015; Villanova, Heberle & Chieregati, 2017; Dominy et al., 2021; Chieregati et al., 2023).

A single DSA test was undertaken, raising the question of repeatability. Such tests (e.g. DSA or HT) are rarely duplicated given their cost and complexity. However, where repeats on the same mineralisation have been undertaken, in the experience of the authors, the results are often quite different. In addition, care must be taken during interpretation of the results, as it is unlikely that the calculated K value is constant through a given mineralisation style or domain(s) (Dominy, Glass & Purevgerel, 2022). If a low value of K is selected then a protocol may be inappropriate, and alternatively if a high K value is selected the protocol may be too complex and costly. This emphasises the need to determine the critical grade(s) at which optimisation should take place.

PhotonAssay[™] offers capability for repeat calibration experiments when combined with an automated fragment group selector such as that proposed by Prado et al., 2024. In this case, the standard (grouped) heterogeneity test is used (Dominy & Xie, 2016; Pitard, 2019; Chieregati et al., 2023). The screened calibration sample is passed through an automated system that selects fragment-by-fragment 50 groups for assay. The advantage with the non-destructive PhotonAssay[™] method, is that groups can be assayed and then recombined for repeat tests on the same material.

Post-testwork, the company is continuing to consider the use of PhotonAssayTM. Currently, it crushes whole 1 m (\pm 0.2 m) NQ2 core composites (approx. 4.5–6.5 kg) to P80 2 mm, rotary splits off 2 kg, which is entirely pulverised and split into two 1 kg lots for SFAs.

4. Discussion

Sampling errors across the mine value chain generate both monetary and intangible losses. At the project development stage these losses can relate to biased resource/reserve estimates, potential project delay and/or wasted/misused capital. During mine operation, issues principally relate to ore/waste misclassification and poor reconciliation. In all cases, there are monetary costs in correcting protocols. Getting sampling correct the first time is a convincing activity.

PhotonAssay™ is a significant development in the gold assaying field. It is a novel X-ray method that provides fast, accurate, fully automated and non-destructive measurements on large samples. The method is agnostic to material composition and granulometry. No chemicals are used, and no waste produced, other than the sample material that can be stored or used again as required. PhotonAssay[™] provides faster turnaround times and lower costs than most analytically competing approaches. Sample material does not require pulverising and can be assayed in a crushed form, generally P80-90 2-3 mm. This provides distinct advantages in terms of time and cost. The method has been ISO/NATA certified, and results have been included in Exploration Results and Mineral Resource/Reserve estimates reported in accordance with the JORC Code and NI 43-101 (Dominy et al., 2022).

Whilst this paper has focused on the sampling of diamond core and RC chips, the discussions are relevant to all sample types, including those used in the underground environment (e.g. chip or channel samples) and/or metallurgical samples (Dominy, 2017; Dominy et al., 2018a,b; Dominy et al., 2023).

Based on the review of data for several global projects, the authors note that for fine gold mineralisation (<100 μ m) the agreement between FA30 and PA500 is good, with grades below 10–15 g/t Au displaying an agreement with ±10%. In some cases, this agreement may increase to more than ±10% if the effect of very minor coarse gold comes into play. Similarly, in the case of coarse gold–bearing mineralisation (>100 μ m), the agreement between FA30 and PA500 is likely to be greater than ±20% given the inherent heterogeneity of the mineralisation. Where PA500 is compared to SFA1000 the agreement is reasonable and within ±20%.

Based on Case Study 1, where D1 mineralisation contains fine disseminated gold, PhotonAssay[™] adds no significant advantage though allows larger samples to be obtained with reduced sample preparation. For coarse gold mineralisation, such as the D2 mineralisation, PhotonAssay[™] of a larger assay charge size using multiple jars is advantageous.

Pulverisation can be applied to reduce the gold particle size and hence the FSE if required. However, care must be taken to avoid gold loss/smearing (PE) and/or promoting GSE.

The practitioner must review the entire "rig-to-assay" process, as simply increasing the assay charge size may not provide the error improvement desired. The primary rig-splitting error may pervade the process. Similarly, the post-crush split in the laboratory may also carry a significant error.

Coarse-gold assaying with FA is flawed (Royle, 1989; Pitard & Lyman, 2013; Dominy, 2014; Dominy, 2017; Dominy et al., 2017; Lyman, Robertson & Day, 2016; Pitard, 2017). The approach is prone to high ISE and CSE, particularly when the assay charge is scooped from the pulp (Dominy, 2016; Minnitt, Dominy & Esbensen, 2022). The propensity of gold not to pulverise efficiently potentially promotes high FSE and GSE effects during sub-sampling for the FA charge.

A whole sample assay method like the PhotonAssay[™] offers an optimised alternative to most currently competing analytical approaches. Inappropriate sampling protocols for coarse gold-bearing mineralisation will unavoidably lead to strong bias and poor precision. Protocols may involve pulverisation of an entire sample, which results in gold liberation. In such cases, sample splitting becomes a critical success factor, and will be highly problematic other than with a riffle splitter or RSD. Any attempt at 'homogenisation' will be useless and will promote GSE instead. Mat mixing or scooping from a pile of pulp or pulveriser bowl, should be avoided with extreme prejudice (Minnitt, Dominy & Esbensen, 2022). There is no escaping the general conclusion that a large-sample assay method such as PhotonAssay[™] is likely to be optimal in the presence of coarse gold.

Future application of PhotonAssay™ will see it integrated into workflows that develop total deposit knowledge in support of geometallurgical programmes. Whilst its analytical capability is currently limited to gold, gold-silver and copper, scanning of the jars by micro-XRF, XCT and spectral sensors will add value. Pre-jarring determinations may include sub-sampling for other assays or tests. The non-destructive nature of PhotonAssay™ allows assayed material to be recombined for other assays or tests across the mineralogical, geochemical, geoenvironmental and metallurgical domains (Arrowsmith, Parker & Dominy, 2018; Dominy et al., 2023). Aspects of the workflow may well be automated. The relevance of real-time data is becoming important to drive more efficient and cost-effective operations globally. Workflows including PhotonAssay™ will contribute to this need. The application of TOS is paramount to achieve quality data through representative samples.

5. Recommendations for the Practitioner

- The CP/QP needs to act and not simply accept "standard" or so-called "best practice" protocols and methodologies for the sampling of gold mineralisation, particularly in the presence of coarse gold. The optimisation of a sampling protocol comes from understanding the mineralisation and desired programme outputs. It is not simply a mathematical, or a statistical process but a complex process taking advantage of orebody knowledge and application of TOS. Follow the general lot-to-aliquot stipulations of first eliminating all ISE effects before addressing GSE and FSE. Then use duplicate pair analysis to assess on-going performance.
- Sampling protocol design must consider programme aim and objective(s) in context of the mineralisation type. In most cases, a dedicated characterisation programme is required to support realistic application of TOS. A "smart" data-collaborative approach to optimisation includes understanding the mineralisation and its sampling needs (Dominy, Xie & Platten, 2008; Dominy, et al., 2021; Dominy, Glass & Purevgerel, 2022; Pitard, 2015; Villanova, Heberle & Chieregati, 2017). Characterisation must start as soon as mineralisation is encountered by outcrop (surface or underground) and/or drilling. Characterisation with respect to gold particle sizing, mineralogy and heterogeneity is critical. Detailed core logging and/or geological mapping will reveal much about the presence of coarse gold and clustering. Initial assaying campaigns should utilise SFA to identify the presence of coarse gold. Preliminary dl and/or dℓclus values may be estimated.
- In the coarse gold environment, calibration approaches such as the HT or DSA are likely to be inappropriate due to the selected primary mass being unrepresentative. Similarly, the results of repeat or multiple tests, which are seldom undertaken, may show substantial differences (Dominy & Xie, 2016; Dominy, 2016; Dominy, Glass & Purevgerel, 2022). Where possible, a priori data should be used during planning to investigate the representative sample mass required and post-calibration for validation of results. In addition, care must be taken during interpretation of the results, as there is no guarantee that the calculated K value is constant through a given mineralisation style or domain(s), notwithstanding changes in grade. This again emphasises the need to determine the critical grade(s) at which optimisation should take place.

- A well-drilled and collected RC sample provides a large mass (>30 kg/m versus 4-8 kg/m for diamond core). Larger splits at the rig are required, supported by a larger assay charge. The CP/QP must consider the relative pros and cons, and design an appropriate "rig to assay" protocol.
- Whole diamond core sampling followed by full sample assay via PhotonAssayTM, SFA, LW or PAL may be required in some cases. This effectively yields zero FSE and GSE values. Arguments against whole core sampling revolve around no reference core remaining, though with modern digital photography, geochemical and spectral sensors, and detailed logging this should not be an issue.
- During mass and sample size reduction at any stage of the process, the split size and mass must be empirically optimised to reduce the FSE, and the correct splitter used to minimise bias. Riffle or RSD type splitters are appropriate as either bench top or automated units (Petersen, Dahl & Esbensen, 2004). Like any piece of sampling equipment, an RSD or riffle splitter must be set up properly and operated correctly (Petersen, Dahl & Esbensen, 2004; Esbensen & Wagner, 2017; Esbensen, 2020). Any kind of scooping or grabbing is likely to lead to high bias. Crush quality and split precision must be monitored as part of the QC process.
- Conducting systematic QC programmes to measure the reliability of each of the sampling, preparation and assaying steps and then optimise the process. QC cannot be divorced from the TOS and is a mandatory step in representative fit-for-purpose sampling. Proper documentation, staff training and periodic peer review are required. Full and open communications are required with laboratory service providers – the CP/QP must visit the laboratory.
- There is a need, and a clear advantage, in moving towards full quantification of errors for objective QC assessment, where a first step is the application of the RSV sampling plus analysis variability characteristic as defined in DS3077 (2013; 2024). Resolution of individual relative errors across the complete sampling, preparation, and analysis stages can be gained from duplicate sample pairs.

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References

Abzalov, M. Quality control of assay data: a review of procedures for measuring and monitoring precision and accuracy. Explor. Mining. Geol., 2008, 17, 131–144.

Arrowsmith, V.; Parker, B.; Dominy, S.C. Beatons Creek conglomerate gold project, Pilbara, WA: sulphide mineralisation metallurgical testwork report. Unpublished internal report, Novo Resources Corporation, 30 April 2019, pp. 69.

Carrasco, P.; Carrasco, R.; Jara, E. The economic impact of correct sampling and analysis practices in the copper mining industry. Chemom. Intell. Lab. Syst. 2004, 74, 209–213.

Carswell, J.T.; Yulia, K.; Lesmana, D.; Steamy, K. Grade control sampling quality assurance/quality control in a high-grade gold mine – Gosowong, Indonesia. In Proceedings of the International Mining Geology Conference; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2009; pp 285–290.

Chieregati, A.C.; Prado, G.C.; Fernandes, F.L.; Villanova, F.L.S.P.; Dominy, S.C. A Comparison between the standard heterogeneity test and the simplified segregation free analysis for sampling protocol optimisation. Minerals, 2023, 13, 680. https://doi.org/10.3390/min13050680

Chrysos, 2020. Procedure for Re-jarring Certified Reference Material (CRM) Jars. Work Instruction: WI-023 – Re-jarring CRMs. Chrysos Corp. internal report, dated April 2020, Version 1. pp. 3.

Chrysos, 2022a. Performance Note PN-001: Chrysos PhotonAssay™ Measurement Performance for PAAU02. Chrysos Corp. internal report, dated April 2022. pp. 2.

Chrysos, 2022b. Technical Note TN-401: QAQC Procedures for Chrysos PhotonAssay™ Systems. Chrysos Corp. internal report, dated December 2022, Version 1. pp. 9.

Chrysos, 2023a. Technical Note TN-003: Chrysos PhotonAssay™ Monitoring Standard Recommendations. Chrysos Corp. internal report, dated March 2023, Version 2. pp. 5.

Chrysos, 2023b. Chrysos Corporation Q1 Financial Year 2024 – Quarterly Investor Update. Chrysos Corp. investor presentation, dated 26 October 2023, pp. 19.

Cintra, E.C.; Scabora, J.A.; Viegas, E.P.; Barata, R.; Maia, G.F. Coarse gold sampling at Sao Francisco mine, Brazil. In Proceedings of the World Conference on Sampling and Blending, Porto Alegre, Brazil, 23–25 October 2007; Fundacao Luiz Englert: Porto Alegre, Brazil, 2007; pp. 187–197.

Clark, I.; Dominy, S.C. Underground bulk sampling, uniform conditioning and conditional simulation – unrealistic expectations. In Proceedings of the Eighth World Conference on Sampling and Blending. Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2017; pp. 3-19.

Dominy, S.C. Grab sampling for underground gold mine grade control, J. South. Afr. Inst. Min. Metall., 2010, 110, 277-287.

Dominy, S.C. Predicting the unpredictable – evaluating high-nugget effect gold deposits. In Mineral Resource and Ore Reserve Estimation Guide to Good Practice; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2014; pp. 659-678.

Dominy, S.C. Importance of good sampling practice throughout the gold mine value chain. Mining Tech. 2016, 125, https://doi.org/ 10.1179/1743286315Y.0000000028

SSI · ISSUE 1 · JANUARY 2024

Dominy, S.C. Sampling coarse gold-bearing mineralisation – developing effective protocols and a case study from the Ballarat mine, Australia. In Proceedings of the World Conference on Sampling and Blending, Perth, Australia, 9–1 May 2017; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2017; pp. 71–84.

Dominy, S.C.; Annels, A.E.; Johansen, G.F.; Cuffley, B.W. General considerations of sampling and assaying in a coarse gold environment. Trans Inst. Min. Metall. (Section B) [App. Earth Sci.], 2000, 109, 145–167.

Dominy, S.C.; Petersen, J.S. Sampling coarse gold-bearing mineralisation-developing effective protocols and a case study from the Nalunaq mine, Southern Greenland. In Proceedings of the World Conference on Sampling and Blending, Sunshine Coast, Australia, 10–12 May 2005; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2005; pp. 151–165.

Dominy, S.C.; Platten, I.M. Clustering of gold particles and implications for sampling. Appl. Earth Sci. 2007, 116, 130-142.

Dominy, S.C.; Xie, Y.; Platten, I.M. Gold particle characteristics in vein deposits: implications for evaluation and metallurgy. In Proceedings of the Narrow Vein Mining Conference, Ballarat, Australia, 14–15 October 2008; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, pp. 91–104.

Dominy, S.C.; Platten, I.M.; Howard, L.E.; Xie, Y.; Bell, R.F.; Minnitt, R.C.A. Determination of the sampling liberation diameter in a high-grade coarse gold ore by high-resolution X-ray computed tomography. In Proceedings of the Sampling Conference, Perth, Australia, 21–22 August 2012; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2012; pp. 161–169.

Dominy, S.C.; Xie, Y. Optimising sampling protocols via the heterogeneity test: challenges in coarse gold. Mining Tech. 2016, 125, https://doi.org/10.1179/1743286315Y.0000000011

Dominy, S.C.; Glass, H.J.; Lam, C.K.; O'Connor, L.; Purevgerel, S.; Minnitt, R.C.A. 2018a. Integrating the Theory of Sampling into underground grade control strategies. Minerals, 2018, 8, 232, https://doi.org/10.3390/min8060232.

Dominy, S.C.; O'Connor, L.; Glass, H.J.; Purevgerel, S.; Xie, Y. 2018b. Towards representative metallurgical sampling and gold recovery testwork programmes. Minerals, 2018, 8, 193, https://doi.org/10.3390/min8050193.

Dominy, S.C.; Graham, J.C. Beatons Creek gold project, Nullagine, WA: grade control programme. Unpublished internal report, Novo Resources Corporation, 29 November 2020, pp. 183.

Dominy, S.C.; Purevgerel, S.; Esbensen, K.H. Quality and sampling error quantification for gold mineral resource estimation. Spectroscopy Europe, 2020, 32(6), 21–27.

Dominy, S.C.; Graham, J.C. Beatons Creek gold project grade control programme – Stage 1 sensitivity and optimisation: analysis and recommendations. Unpublished internal report, Novo Resources Corporation, 2 November 2021, pp. 120.

Dominy, S.C.; Platten, I.M.; Glass, H.J.; Purevgerel, S.; Cuffley, B.W. Determination of Gold Particle Characteristics for Sampling Protocol Optimisation. Minerals, 2021, 11, 1109. https://doi.org/10.3390/min11101109

Dominy, S.C.; Glass, H.J.; Purevgerel, S. Sampling for resource evaluation and grade control in an underground gold operation: a case of compromise. TOS forum, 2022, 11, 375–396. https://doi.org/10.1255/tosf.165

Dominy, S.C.; van Roij, A.; Graham, J.C. Sampling of high-nugget conglomerates from the Western Australian Pilbara: Bulk sampling at the Beatons Creek gold project, Nullagine. TOS forum, 2022, 11, 255-277. https://doi.org/10.1255/tosf.155

Dominy, S.C.; Graham, J.C.; Ison, J.; McAuslane, R. Mineral Resource update: Beatons Creek gold project, Nullagine, Western Australia. NI 43–101 Technical Report, Novo Resources Corporation, 30 June 2022, pp. 210.

Dominy, S.C.; Parker, B.; van Roij, A.; Graham, J.C.; Glass, H.J.; Purevgerel, P. Geometallurgical testwork protocol for coarse gold mineralisation utilising PhotonAssay™. Presented at the IOM3 Geometallurgy Conference 2023, London, December 2023.

DS3077. Representative Sampling - Horizontal Standard. 2.ed. Danish Standards Foundation, Copenhagen, 2013, 41 p.

DS3077. Representative Sampling - Horizontal Standard. 3.ed. Danish Standards Foundation, Copenhagen, 2023 (in prep)

Esbensen, K.H. Introduction to the Theory and Practice of Sampling; IM Publications: Chichester, United Kingdom, 2020; p. 328.

Esbensen, K.H.; Minkkinen, P.; Holmes, R.J.; Dominy, S.C.; Vogel, D.A.; Romanach, R.J.; Robben, C.; Dehaine, D.; Paoletti, C.; Engstrom, K.; et al. Economic arguments for representative sampling. Spectroscopy Europe, 2021, 33(7), 1–88. https://doi.org/10.1255/sew.2021.a30.

Esbensen, K.H.; Wagner, C. Representative mass reduction in the laboratory: riffle splitting galore (with or without errors). Spectroscopy Europe, 2017, 29(1), 20–26.

François-Bongarçon, D.M. Extensions to the demonstration of Gy's formula. Explor. Min. Geol. 1998, 7, 149-154.

François-Bongarçon, D.M. Theory of sampling and geostatistics: An intimate link. Chemom. Intell. Lab. Syst. 2004, 74, 143-148.

François-Bongarçon, D.M.; Gy, P.M. The most common error in applying Gy's formula in the theory of mineral sampling and the history of the Liberation factor. J. South. Afr. Inst. Min. Metall. 2002, 102, 475–479.

Gy, P.M. Sampling of Particulate Materials: Theory and Practice; Elsevier: Amsterdam, The Netherlands, 1982; p. 431.

Howard, L.E.; Elangovan, P.; Abel, R. L.; Dominy, S.C.; Armstrong, R. Characterisation of gold ores by X-ray micro-computer to-mography part 1: software for calibration and quantification of mineralogical phases. In Proceedings International Geometallurgy Conference, Brisbane, Australia, 5–7 September 2011; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, pp. 321–330.

Huffman, E.L.; Clark, J.R.; Yeager, J.R. Gold analysis – Fire assaying and alternative methods. Exploration and Mining Geology, 1999, 7, 155–160.

Johansen, G.F.; Dominy, S.C. Development of sampling protocols at the Bendigo gold project, Australia. In Proceedings of the World Conference on Sampling and Blending, Sunshine Coast, Australia, 10–12 May 2005; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2005; pp. 175–183.

Kyle, J.R.; Ketcham, R.A. Application of high-resolution X-ray computed tomography to mineral deposit origin, evaluation and processing. Ore Geol. Rev., 2015, 65, 821–839.

Lyman, G.J. Theory and Practice of Particulate Sampling – an engineering approach. Materials Sampling and Consulting: Southport, Australia, 2019; p. 540.

Lyman, G.J. Statistical theory for sampling of particulate materials. Minerals, 2023, 13, 905. https://doi.org/10.3390/min13070905

Lyman, G.J.; Bourgeois, F.S. Sampling, corporate governance and risk analysis. In We are Metallurgists not Magicians: Landmark Papers by Practicing Metallurgists; The Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2017; pp. 349–354.

Lyman, G.J.; Robertson, I.G.; Day, T. The simple facts about sampling gold ores. In Proceedings of the Mill Operators Conference, Perth, Australia, 10–12 October 2016; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2016; pp. 159–172.

Minnitt, R.C.A. Sampling: The impact on costs and decision making. J. South. Afr. Inst. Min. Metall. 2007, 107, 451-462.

Minnitt, R.C.A. The Grouping and Segregation error in the rice experiment. Minerals, 2022, 12, 335, https://doi.org/10.3390/min12030335

Minnitt, R.C.A.; Rice, P.; Spangenberg, C. Experimental calibration of sampling parameters K and alpha for Gy's formula by the sampling tree method. J. S. Afr. Inst. Min. Metall. 2007, 107, 513–518.

Minnitt, R.C.A.; Assibey-Bonsu, W. A comparison between the duplicate series method and the heterogeneity test as methods for calculating Gy's sampling constants, K and alpha. In Proceedings of the World Conference on Sampling and Blending, Cape Town. Southern African Institute of Mining and Metallurgy. 2009, pp. 137-154.

Minnitt, R.C.A.; François-Bongarçon, D.M.; Pitard, F.F. Segregation Free Analysis for calibrating the constants K and α for use in Gy's formula. In Proceedings of the World Conference on Sampling and Blending, Santiago, Chile, 25–28 October 2011; GECA-MIN: Santiago, Chile, 2011; pp. 133–150.

Minnitt, R.C.A.; Dominy, S.C.; Esbensen, K.H. Mixing is a double-edged sword: the grouping and segregation error on the assayer's bench. Spectroscopy Europe, 2022, 34(1), 30-39.

SSI · ISSUE 1 · JANUARY 2024

OREAS, 2023a. Au PhotonAssay™ Recertification, news release dated 4th July 2023 from Ore Research & Exploration Pty Ltd, Australia.

OREAS, 2023b. Justification and impact of PhotonAssay™ recertification of 15 OREAS CRMs. Technical note from Ore Research & Exploration Pty Ltd dated 9th August 2023. pp. 4.

Petersen, L.; Dahl, C.; Esbensen, K.H. Representative mass reduction in sampling - A critical survey of techniques and hardware. Chemom. Intell. Lab. Syst., 2004, 74, 95–114.

Pitard, F.F. The in-situ nugget effect: A major component of the random term of a variogram. In Proceedings of the World Conference on Sampling and Blending, Porto Alegre, Brazil, 23–25 October 2007; Fundacao Luiz Englert: Porto Alegre, Brazil, 2007; pp. 91–110.

Pitard, F.F. Guidelines for acceptable allotted sampling uncertainty. In Proceedings of the World Conference on Sampling and Blending; Santiago, Chile, 10–12 July 2013; Gecamin, Santiago, Chile, 2013, pp. 89–98.

Pitard, F.F. The advantages and pitfalls of conventional heterogeneity tests and a suggested alternative. TOS forum, 2015, 5, 13–18.

Pitard, F.F. From errors to uncertainty – a clarification for proper use by the Theory of Sampling. In Proceedings of the World Conference on Sampling and Blending, Perth, Australia, 9–1 May 2017; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2017; pp. 355–358.

Pitard, F.F. Theory of Sampling and Sampling Practice; CRC Press: Boca Raton, FL, USA, 2019; p. 694.

Pitard, F. F.; Lyman, G.J. Single and multi-stage Poisson processes: a case study for gold exploration, Proceedings of World Conference on Sampling and Blending, Santiago: Gecamin, 2013, 371–385.

Prado, G.C.; Chieregati, A.C.; Pitard, F.F.; Dominy, S.C. An automated alternative for heterogeneity testing. Minerals, 2024, in review.

Royle, A.G. Splitting gold assay pulps containing coarse gold. J. Leeds Univ. Min. Assoc., 1989, 89, 63–68.

Simon, A.; Gosson, G. Considerations on quality assurance/quality control and sample security. In Proceedings of the Sampling Conference, Perth, Australia, 27–29 May 2008. Australasian Institute of Mining and Metallurgy, 2008, 135–140.

Stanley, C.R.; Lawrie, D. Average relative error in geochemical determinations: clarification, calculation and plea for consistency. Explor. Mining. Geol., 2007, 16, 265–274.

Stanley, C.R.; Smee, B.W. Strategies for reducing sampling errors in exploration and resource definition drilling pro-grammes for gold deposits. Geochem. Explor. Env. Anal. 2007, 7, 1-12.

Tickner, J. Commercial analysis of gold ores via photonuclear activation. IRPS Bulletin, 2021, 34(1), 6-12.

Tickner, J.; Ganly, B.; Lovric, B.; O'Dwyer, J. Improving the sensitivity and accuracy of gamma activation analysis for the rapid determination of gold in mineral ores. Applied Radiation and Isotopes, 2017, 122: 28–36.

Tickner, J.; Preston, R.; Treasure, D. Development and operation of PhotonAssay system for rapid analysis of gold in mineral ore. In Proceedings ALTA Conference. 2018, pp. 11.

Tremblay, C.D.; Tickner, J.; Treasure, D.; Oteri, A.; Wheeler, G. PhotonAssay – efficient and bulk gold analysis in the modern world. In Proceedings of the International Mining Geology Conference, Perth, Australia, 25–26 November 2019; Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2019; pp. 88–98.

Tremblay, C.D.; Wheeler, G.; Oteri, A. PhotonAssay – efficient and bulk gold analysis in the modern world. In Proceedings for the AEGC 2019 Data to Discovery Conference. 2019, pp. 4. https://doi.org/10.1080/22020586.2019.12073071

Villanova, F.L.S.P.; Heberle, A.; Chieregati, A.C. Heterogeneity tests and core logging—A final reconciliation. In Proceedings of the World Conference on Sampling and Blending, Perth, Australia, 9–11 May 2017; The Australasian Institute of Mining and Metallurgy: Melbourne, Australia, 2017; pp. 107–113.

Appendix

Tab. A1: Definition of TOS sampling errors.

Sampling error	Acronym	Error type	Effect on sampling	Source of error	Error definition
Fundamental	FSE	Correct Sampling Error (CSE)	Random Errors – Precision Generator	Characteristics of mineralisation. Relates to Constitution and Distribution Hetero- geneity	Grade heterogeneity of the broken lot. FSE does not cancel out and remains even after a sampling operation is perfect. Experience shows that the total nugget effect can be artificially high because sample weights are not optimal.
Grouping and Segregation	GSE	ng Error (CSE)			Error due to the combination of grouping and segregation of rock fragments in the lot. Once rock is broken, there will be segregation of particles at any scale.
Delimitation	IDE		Systematic Errors – Bias Generator	Sampling equipment and materials handling	Incorrect shape of the volume delimiting a sample.
Extraction	IEE	Incorrect Sampling Error (ISE)			Incorrect extraction of a sample. Extraction is only correct when all fragments within the delimited volume are taken into the sample.
Weighting	IWE				Collection of samples that are of comparable support. Samples should represent a consistent mass per unit.
Preparation	IPE				Issues during sample transport and storage (e.g. mix-up, damage), preparation (contamination and/or losses), and intentional (sabotage) and unintentional (careless actions and non-adherence of protocols) human error.
Analytical	TAE	Analytical		Analytical process	Errors during the assay and analytical process, including issues related to rock matrix effects, human error, and analytical machine maintenance and calibration.

Tab. A2: Abbreviations used in this manuscript.

TAE Total analytical error

CP Competent Person (e.g. JORC, PERC, etc.)

CRM Certified reference material
CSE Correct sampling error

IDE Increment delimitation error
DSA Duplicate series analysis

 $\mathrm{d}\ell$ / $\mathrm{d}\ell_{\mathrm{clus}}$ Liberation diameter for sampling purposes, particle vs. clustered value

dN Nominal particle size (95% passing / 5% retained)

IEE Increment extraction error
ESD Equivalent spherical diameter

FA Fire assay (assay charge size 30 g; FA30)

FSE Fundamental sampling error

GRAV Gravity assay method

GSE Grouping and segregation error

ISE Incorrect sampling error

K Sampling constant

LDL Lower detection limit

LINAC Linear accelerator

LW LeachWELL (assay charge size 1,000 g; LW1000)

NQ/NQ2 Diamond drill core size (47.6 mm and 50.5 mm respectively)

PA PhotonAssay™ (assay charge size 500 g; PA500)

PAAU02 PhotonAssay™ 2-cycle analysis

PAL Pulverise and leach (assay charge size 500 g; PAL500)

IPE Increment preparation error

P₈₀, etc. Percent passing (e.g., P₈₀; 80% passing a given screen size)

QAQC Quality assurance/quality control

QFE1 Quality fluctuation error (component #1)

QP Qualified Person (e.g. NI 43-101)

RC Reverse circulation (drilling)

ROM Run-of-mine

RSD Rotary sample divider

RSV Relative sampling variability (same as COV: coefficient of variation)

SD Standard deviation

SFA Screen fire assay (assay charge size 500 g; SFA500)

SNE Sampling nugget effect (component)

TOS Theory of Sampling
TSE Total sampling error
IWE Increment weighting error

XCT X-ray computed tomography