CHRYSOS
CORPORATION
Assays at the speed of light

Technical Note TN-101

PhotonAssay™ Measurement Performance for Gold on Ore Samples

Sample preparation and fire-assay comparisons

Executive Summary

Gold presents unique analysis challenges, as it is mined commercially at very low concentrations, is often distributed very irregularly, and can be difficult to sample due to its malleability and resistance to pulverisation. Traditional methods such as fire-assay and cyanide leach are labour intensive, relatively slow and require the use of toxic or caustic reagents.

PhotonAssay™ provides a novel method for the rapid, automatic and non-destructive analysis of gold and other metals in mineral samples. Using high-power X-rays to activate and measure any gold atoms present, the technique allows a true bulk analysis of large samples (typically 500 g) and is insensitive to the chemical or physical form of the material being assayed.

In this report, we explore the application of PhotonAssay™ to the measurement of gold in real mineral samples sourced from Australian and international operations. In aggregate, nearly 12,000 measurements on approximately 2,000 separate materials have been performed.

This report tackles three main questions:

- Does PhotonAssay™ provide comparable results to the widely-accepted, industry-standard method of fire-assay?
- How is the accuracy of the PhotonAssay™ method affected by different sample preparation protocols?
- What level of sample preparation is required for PhotonAssay™ to achieve similar or better levels of accuracy than conventional fire-assay?

We find that the analysis results obtained using PhotonAssay™ of drill core, reverse circulation drilling and coarse reject materials crushed to a top-size of 2-3 mm are strongly correlated with those obtained using fire-assay. Statistical tests suggest that the two analysis techniques can be used interchangeably during a drilling program.

Analysis of the repeatability of PhotonAssay™ measurements performed using multiple aliquots sampled at different material top-sizes for a range of drill-sites and deposit types indicate that combined sampling plus instrumental errors for PhotonAssay™ on 2-3 mm top-size crushed ores are generally comparable to those obtained using fire-assay on pulverised samples.

By analysing a sample mass ten times that used for a traditional fire-assay, the sampling variance is often decreased, providing immediate benefit to geologists. This allows the sample preparation protocol to be simplified, generating immediate benefits in cost and time savings.

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Introduction

The Chrysos PhotonAssay^{TM} method provides an alternative to traditional chemical methods for measurement of gold in mineral ores. PhotonAssay^{TM} uses high-energy, high-power x-rays to activate gold atoms inside large samples with a typical mass of 500 g. Samples are placed into sealed, barcoded plastic jars in which they remain throughout the analysis process. Gamma-rays of characteristic energy emitted by the activated gold are measured and counted to estimate the gold content of the sample. The method takes 2-3 minutes to complete, is non-destructive and fully automated. The high energies of the source x-rays and activation gamma-rays make them highly penetrating, meaning that the entire sample mass is analysed.

Fire-assay is the most widely used and accepted traditional method for gold analysis. Small aliquots of material, typically 20-50 g, are mixed with a flux containing lead and other reagents and heated in a furnace. The sample and flux react and melt, resulting in a molten lead layer that ideally contains all the sample's gold, and a glassy slag layer. After cooling, the lead and glass are separated. The gold-bearing lead is then remelted in a semiporous cupel; the lead is absorbed and a metallic prill containing the gold is left behind. The prill is either weighed directly or dissolved in acid and the resulting solution measured via AAS, ICP-OES or ICP-MS to determine the gold concentration.

Previous studies exploring the performance of the PhotonAssay^{TM} method have used certified reference materials (CRMs), whose gold contents have been accurately determined using multi-laboratory fire-assay round-robins. The CRMs are prepared to be highly homogeneous, and so provide a direct measurement of the instrumental accuracy of an analysis technique. These tests demonstrated excellent agreement between PhotonAssay^{TM} and fire-assay, and the insensitivity of the PhotonAssay^{TM} method to the matrix type and chemistry of the sample.

In this report we focus on a comparison of the PhotonAssay^{TM} and fire-assay methods applied to 'real' materials received from Australian and global mining operations. We explore the impact of particle size on both instrument and sampling errors and investigate whether the large sample mass used in PhotonAssay^{TM} allows for sample preparation to be simplified without compromising accuracy.

The main body of the report is organised as follows:

- First, we briefly summarise test work performed on certified reference materials that establishes the analytical performance of the PhotonAssay^{TM} method.
- Next, we present direct comparisons of fire-assay and PhotonAssay^{TM} determinations of gold grade for samples received from both Australian and international operations.
- We then evaluate experimental repeatability errors (precisions) for both fire-assay and PhotonAssay, which provide a measure of sampling and instrumental errors.
- Last, we present conclusions on the efficacy of different techniques for PhotonAssay^{TM} sample preparation.

In an appendix, we briefly introduce some basic elements of gold sampling theory and analyse our measured sampling errors within the framework of the Theory of Sampling.

Validation of PhotonAssay^{TM} on certified reference materials

Extensive testing of the PhotonAssay^{TM} method on certified reference materials (CRMs) has been performed.

CRMs are manufactured materials that have been prepared to be extremely homogeneous. The grade of gold and other elements in these materials is accurately established by a round-robin analysis, with samples sent to a large number of assay laboratories. After statistical removal of outlying results, the certified grade is calculated from the mean of the results returned by the different participating laboratories.

A set of commercial gold analysis services are currently offered on the Chrysos PA1408X system. In the Standard Gold Analysis (SGA) service each sample is run for 2 analysis cycles, resulting in a throughput of 72 assays per hour. Repeat measurement of blank samples over at least 6 months' operation on each deployed unit has demonstrated a 3-sigma lower detection limit of approximately 0.01 ppm. The blank material contains very low levels of uranium, thorium, and barium. Elevated levels of these elements raise the gamma-ray background underneath the gold signal and lead to an increase in detection limit. Consequently, the observed 3-sigma detection limit for gold ores with typical concentrations of these elements is about 0.025 ppm. The precision (1 SD) at 1 ppm gold concentration is 4%, improving to 2.5% at concentrations of 10 ppm and above.

Results from a feasibility study conducted on the first Chrysos PA1408X unit located in Perth are presented in Figures 1 and 2. A suite of 90 CRMs from four suppliers was measured, with each jar undergoing at least 6 2-cycles analyses. A comparison of PhotonAssay^{TM} and certified grades for these materials is shown in Figure 1. The R^2 value for the comparison is 0.9996.

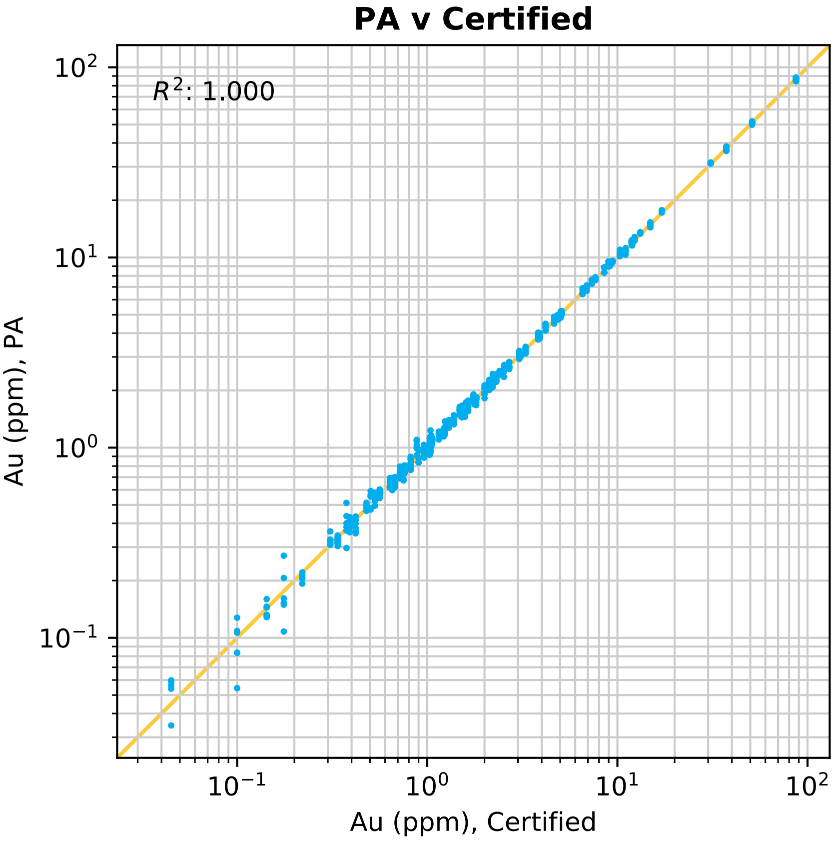

Figure 1. Comparison of PhotonAssay^{TM} gold grades (y-axis) and certified reference grade (x-axis) for 92 CRMs measured using the PhotonAssay^{TM} system operating in Perth, Western Australia.

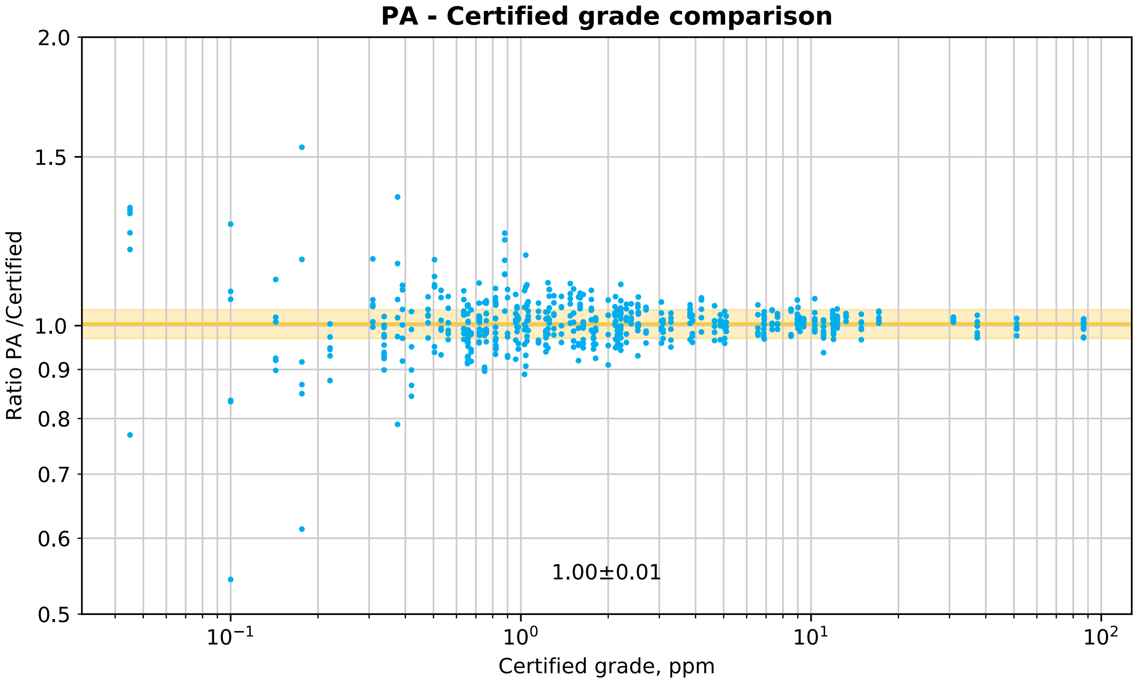

Figure 2. Tukey mean-ratio plot comparing the grades from PhotonAssay™ and fire-assay for the suite of CRMs. The ratio of the paired grades is plotted as a function of the mean sample grade, determined from the average of the two methods. The yellow band indicates the mean ratio and grade ratio variation (±1 SD) averaged over all samples.

The log-weighted mean ratio of the grade ratios is consistent with unity, indicating that PhotonAssay™ and fire-assay can be used interchangeably. The standard deviation in the PhotonAssay™ to fire-assay grade ratios is 3.5%. Assuming a negligible contribution from sampling error or manufacturer uncertainty, this spread provides an estimate of the PhotonAssay™ instrument error.

Figure 3 shows a repeatability chart (process performance chart) for a high-grade CRM measured 150 times over a few months of operation from January to August 2020.

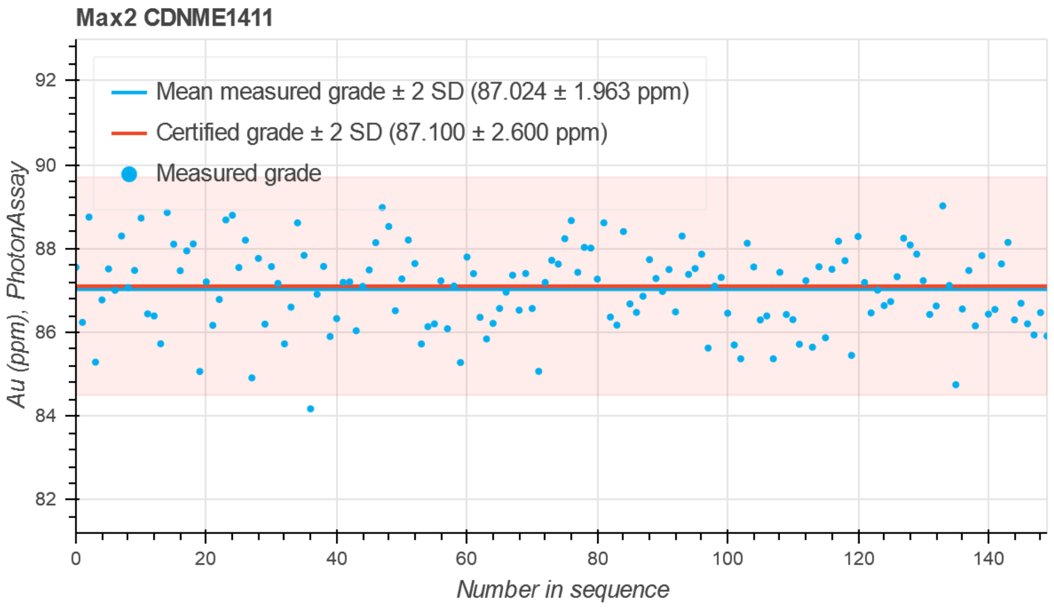

Figure 3. Process performance chart for high grade CRM CDNME1411 (87.1 ppm gold content). Two standard deviation limits, determined from the fire assay SD information provided by the CRM supplier, are shown as the shaded band.

The chart plots individual gold grade measurements as a function of measurement number. The red shaded area denotes the ± 2 standard deviation (SD) limits for fire assay measurements reported by the CRM manufacturer, as determined from inter-lab comparisons. The fire-assay certified mean grade and PhotonAssay-determined mean grade are shown as red and blue lines, respectively.

All measurements lie within ± 2.5 SD of the mean PhotonAssay™ value, indicating the stability and repeatability of the measurement process. The PhotonAssay™ SD value is slightly better than that reported for fire assay measurements, an observation that generally holds for CRMs with grades of a few ppm and above. At grades below 1-2 ppm, the precision of PhotonAssay™ is generally similar to or lower than that of fire-assay due to the higher detection limit of the PhotonAssay™ technique.

Comparison of PhotonAssay™ and fire-assay: factory testing program

The simplest and most direct method to evaluate the performance of PhotonAssay™ on real ore materials is to compare results against a widely used and accepted existing analytical method, namely fire-assay. A preliminary evaluation was performed during initial factory testing of the first PhotonAssay™ system, using materials supplied by gold producers from a range of Australian and international mining operations.

The factory testing program was organised and run by Chrysos staff. Suites of samples were requested from both major international gold producers and smaller Australian companies. Participants in the test program were asked to provide approximately 50 samples of 1 kg mass from materials chosen at their discretion.

Interpretation of these criteria varied significantly, and the received sample suites generally comprised from 20 to several hundred samples, with masses ranging from about 0.5 kg to several kilograms. Received materials ranged from finely pulverised powders (including reference materials) to coarse rock, and included ores, waste, and process materials (see Figure 4). Altogether, approximately 1500 sample aliquots were prepared and measured.

Figure 4. Samples used in factory testing program loaded into standard 100 mm diameter containers; coarse chips (left) and dried process pulps (right). Lids have been removed to illustrate the contents.

Generally, materials were sampled as-received to exhaustion into standard PhotonAssay™ sample containers, which were then sealed and barcoded. As many jars were used as required to hold each sample.

All samples were assayed blind and results sent to the participating companies. The participants arranged conventional assays of the samples and subsequently provided these results to Chrysos for comparison with PhotonAssay™.

Figure 5 plots a comparison of PhotonAssay™ and fire-assay results for two suites of samples with contrasting characteristics. In both cases, the PhotonAssay™ and fire-assay measurements were performed on different sample aliquots, meaning that the result comparisons include contributions from both instrument and sampling errors.

Materials from deposit A were supplied as pulverised powder. They originate from a large-scale, open-pit Peruvian gold mining operation with finely disseminated mineralisation. Approximately 1 kg each of 22 samples was provided, enough to fill 2-4 Chrysos jars. The samples were also analysed via fire-assay, with 4 repeat measurements performed.

Materials from deposit B were supplied as rock chips. They came from a high-grade underground mine located in Victoria, Australia. The deposit contains significant coarse and visible gold. Approximately 0.5 kg of each of 103 samples was received, enough to prepare a single jar from each material. The samples were analysed separately via fire-assay (25 g and 50 g charges) and via screen fire-assay.

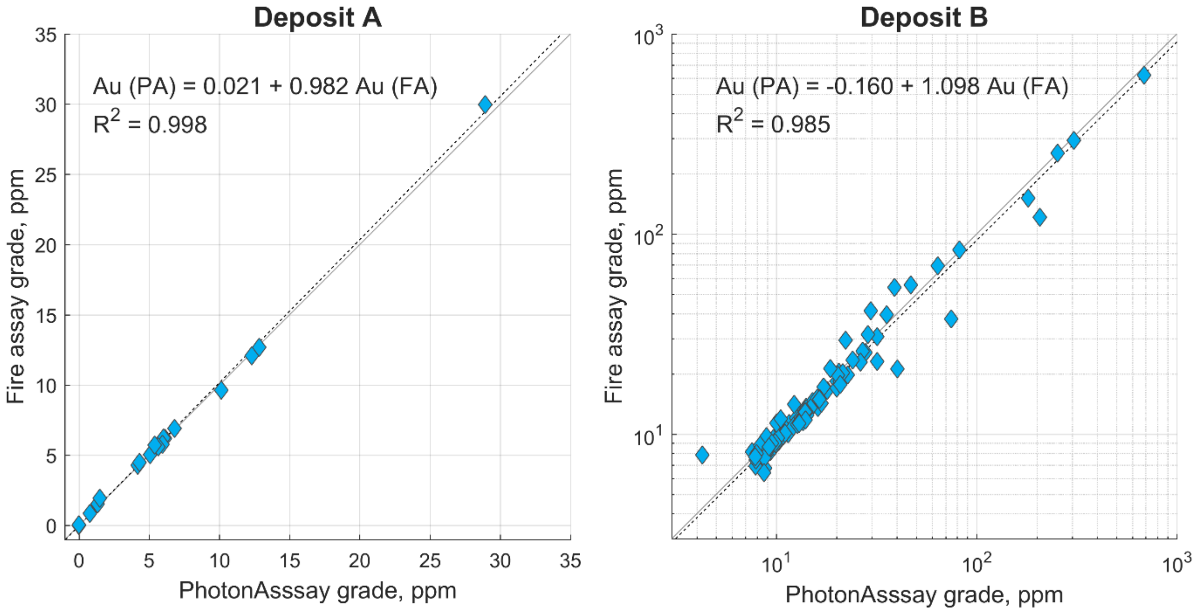

Figure 5. Comparison of PhotonAssay™ and fire-assay results for samples received from deposits in Peru (A) and Victoria, Australia (B).

The left-hand plot in Figure 5 compares PhotonAssay™ and fire-assay results for the Peruvian deposit. The PhotonAssay™ gold values are the average of the results for the 2-4 jars prepared from each sample, and the fire-assay results are the average of the 4 replicate measurements. The correlation between the two analysis methods is extremely good. The right-hand plot in Figure 5 compares the PhotonAssay™ and screened fire-assay results for the Victorian deposit. Due to the wide range of grades spanned in this sample suite, with samples ranging from a few ppm to nearly 700 ppm, a logarithmic scale is used for this plot.

Due to the difficulty in sampling this material, there is considerably more scatter between the two analysis methods, but the overall correlation is still strong. The agreement of the PhotonAssay™ results with those obtained using a screened fire-assay ($R^2 = 0.985$) is better than that with 25 g and 50 g traditional fire-assays ($R^2 = 0.946$ and $R^2 = 0.951$ respectively), indicating that using a larger sample mass is particularly advantageous for this deposit.

The two suites of materials were selected to illustrate the range in the quality of agreement observed between PhotonAssay™ and fire-assay. Similar levels of agreement were observed for the other materials studied during the factory test program, indicating the general suitability of the PhotonAssay™ method for analysis of a wide range of deposit types.

Comparison of PhotonAssay™ and fire-assay: Perth testing program

After the PhotonAssay™ unit was installed and commissioned in Perth, an extensive test program was developed and run in conjunction with the staff of MinAnalytical Laboratory Services in Perth, Western Australia. Materials were sourced from a variety of Australian gold operations and the effects of different material preparation and sampling protocols were investigated in detail.

Materials were sourced from 10 different drill sites in Australia operated by 7 different companies. In total, more than 10,000 sample aliquots were prepared from over 1200 unique bulk samples.

Samples were dried on receipt where necessary, and then variously prepared by crushing and pulverising to explore the impact of different particle top-sizes on sampling errors and analysis accuracy. Aliquots for PhotonAssay™ analysis were drawn from prepared materials with up to four different particle top-sizes:

- RAW samples, prepared from as-received material
- 15 mm top-size, with the as-received material passed through a jaw-crusher
- 2-3 mm top-size, with the 15 mm top-size material passed through a Boyd crusher
- 75 μm top-size, prepared by pulverising the 2-3 mm material using an LM5 mill

Sufficient material was sampled to fill a standard 320 mL PhotonAssay™ jar. The masses of these aliquots typically range from 500-600 g for the RAW, 15 mm and 2-3 mm crushed materials, and 350 g for pulverised materials. Fire-assay aliquots used for comparison measurements were always drawn from pulverised 75 μm material.

Two main types of samples were received: drill-cores (DC) and reverse circulation (RC) chips. Some materials were also supplied as 2-3 mm top-size rejects from samples prepared at other laboratories. Figure 6 and Figure 7 illustrate DC and RC materials in the form received, and after preparation and loading into PhotonAssay™ sample jars.

Different preparation and sampling protocols were developed to explore various aspects of the performance of the PhotonAssay™ technology. These are described in more detail below.

Figure 6. (Left) Dried drill-core samples in trays. (Right) PhotonAssay^{TM} jar of sampled core material after crushing to a top-size of approximately 2-3 mm. (Core image credit: MinAnalytical Laboratory Services.)

Figure 7. (Left) Chip-trays created by RC drilling. (Right) PhotonAssay^{TM} jar of sampled core material after crushing to a top-size of approximately 2-3 mm. (Chip-trays image credit: MinAnalytical Laboratory Services.)

Analysis of identical aliquots using PhotonAssay^{TM} and fire-assay

As PhotonAssay^{TM} is a non-destructive analysis method that leaves the sample physically and chemically unaltered, it is possible to perform multiple measurements using the same physical aliquot. This avoids or minimises issues with sampling different aliquots from an original bulk sample.

Samples from one of the drill-sites were selected and subjected to the following sampling and measurement protocol:

- Material was crushed to a top-size of 2-3 mm
- Two aliquots (500 g approximately) were sampled and analysed via PhotonAssay^{TM}
- Material from each PhotonAssay^{TM} jar was separately removed, pulverised to 75 microns, reloaded into two[1] jars and re-analysed via PhotonAssay^{TM}
- Sufficient pulverised material was removed from each jar to perform a fire-assay.

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[1] Pulverising reduces the effective bulk density of the ore, meaning that two sample jars are required to hold material that previously fitted into a single jar.

This protocol allows for direct comparisons to be made between PhotonAssay^{TM} analyses performed on 2-3 mm and 75 micron top-size material, and between PhotonAssay^{TM} and fire-assay. Figure 8 presents these comparisons, plotting the ratio of two determinations of the gold grade for each sample as a function of the grade determined by fire-assay.

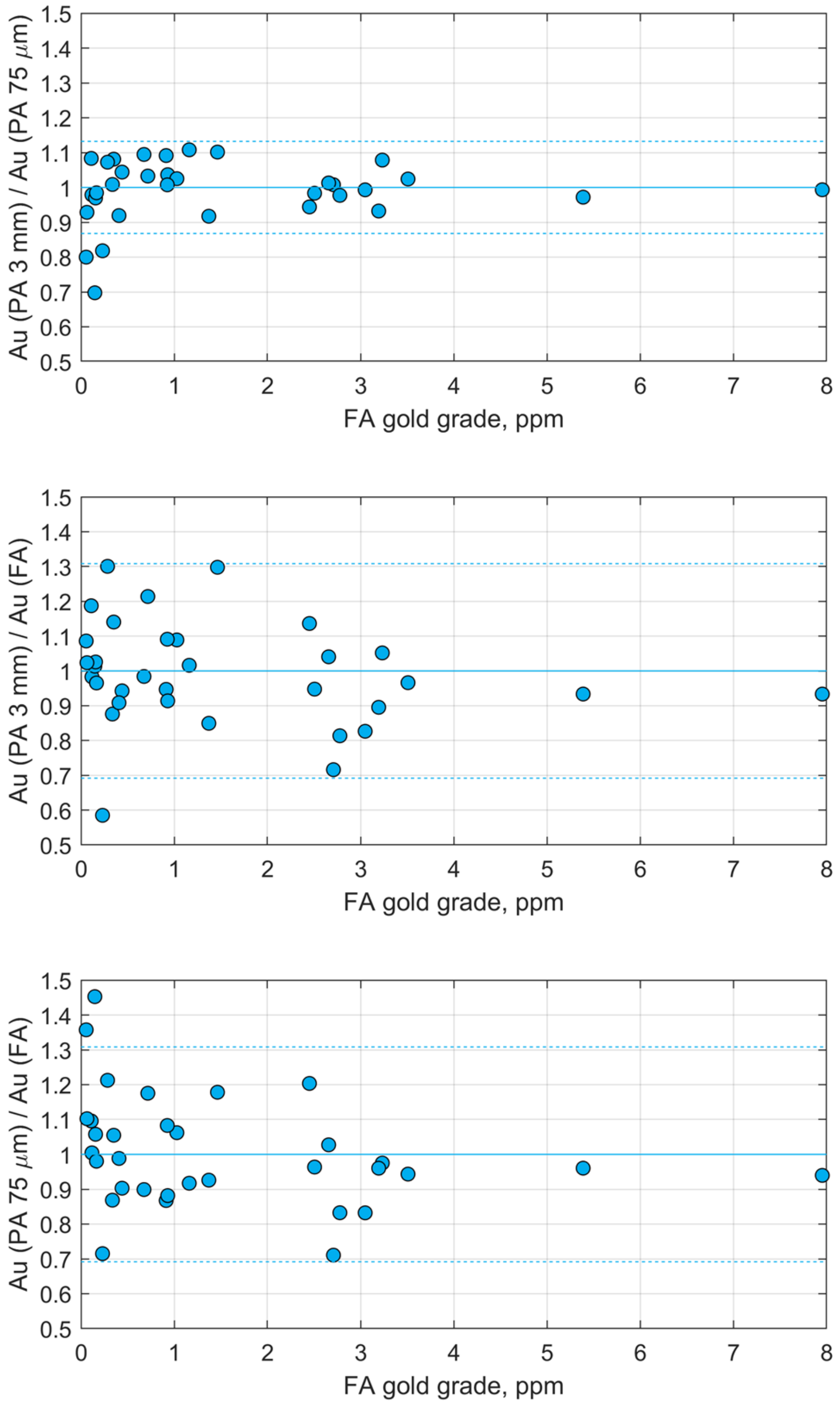

Figure 8. Comparison of PhotonAssay^{TM} and fire-assay analyses performed on the same material aliquot. (Top) Ratio of PhotonAssay^{TM} results on 3 mm top-size ore and on same material after pulverising to 75 microns. (Middle) Ratio of PhotonAssay^{TM} (3 mm top-size) to fire-assay results. (Bottom) Ratio of PhotonAssay^{TM} (75 micron top-size) to fire-assay results. Solid and dotted lines indicate unity ratio and +/-2 SD limits respectively.

The top plot compares the results determined via PhotonAssay^{TM} for 3 mm and 75 micron top-size material. The 3 mm top-size data are the average of the measurements of the two aliquots taken from each sample; the 75 micron top-size data are the average of the measurements of the 4 resulting aliquots obtained after pulverisation. The average relative difference between the two measurements is approximately 6% (1 SD), dominated by instrument error for the low-grade samples (Au concentration < 0.5 ppm). The average value of the grade ratio, 0.992±0.016, is consistent with unity.

The middle plot compares results determined via PhotonAssay^{TM} using 3 mm top-size material to those obtained using fire-assay. The fire-assay data are the average of the results obtained for the 4 samples taken from the jars of pulverised material. A larger spread in the ratio of sample grades is observed, approximately 15% (1 SD). Comparison of the 4 fire-assay measurements performed on each original sample indicate that the spread in the PhotonAssay^{TM}/fire-assay ratio is dominated by sampling of the small fire-assay aliquots (50 g) from the much larger PhotonAssay^{TM} aliquots. The dashed lines indicate the estimated +/- 2SD sampling errors. Again, the average value of the grade ratio (0.991±0.026) is consistent with unity.

Finally, the lower plot compares results determined via PhotonAssay^{TM} using pulverised material (75 micron top-size) to those obtained using fire-assay. A similar spread is observed, with a standard deviation of 16%, which again is dominated by the sampling of the fire-assay aliquots from the larger PhotonAssay^{TM} sample. The average value of the grade ratio is 1.004±0.028.

These results indicate that the PhotonAssay^{TM} analysis is unaffected by the particle top-size size of the sample over a range of 75 microns to 2-3 mm. Further, the results from PhotonAssay^{TM} are in good agreement with those obtained using fire-assay. The spread in the ratios of the PhotonAssay^{TM} to fire-assay grade is mainly accounted for by errors introduced by sampling of the fire-assay aliquots from the larger PhotonAssay^{TM} samples.

Comparison of analyses performed on different sample aliquots

Having established the consistency of the PhotonAssay^{TM} and fire-assay techniques when applied to identical sample aliquots, subsequent measurements were performed on different aliquots drawn from a large bulk sample. This allowed all PhotonAssay^{TM} samples to be preserved for future reanalysis if required.

Materials from the 10 drill sites were prepared and sampled according to the following protocol. From each original bulk sample, duplicate PhotonAssay^{TM} aliquots were drawn from the as-received material with a nominal top-size of 20 mm, from material crushed to 15 mm using a jaw crusher, from material crushed to 2-3 mm using a Boyd crusher, and from material pulverised to 75 μm using an LM5 mill. Separately, 50 g aliquots were also drawn from the pulverised material for analysis via fire-assay. Figure 9 summarises the sampling protocol.

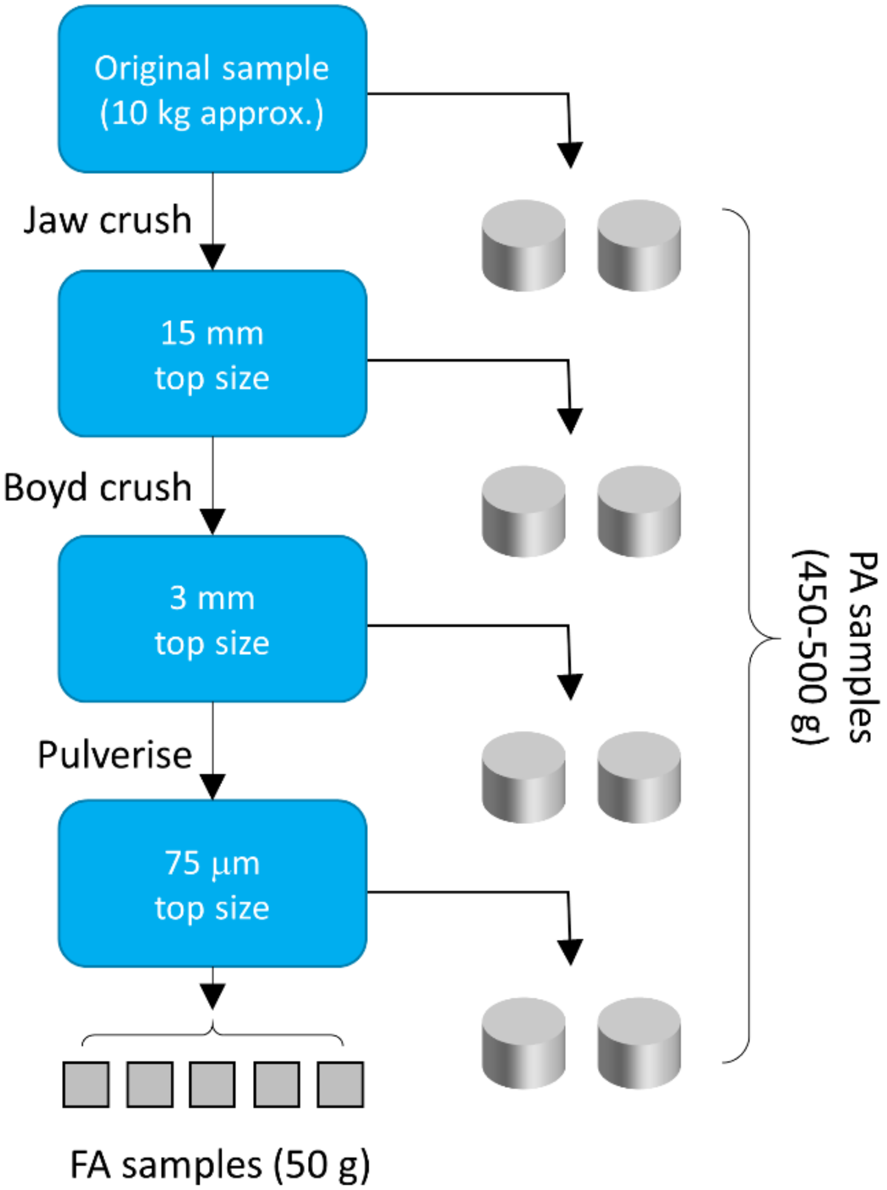

Figure 9. Sampling scheme used for repeatability error determination of PhotonAssay^{TM} and fire-assay methods.

Generally, where the volume of supplied material permitted, two PhotonAssay^{TM} aliquots were prepared from each sample at each particle size. Five fire-assay aliquots were drawn from the final pulverised material and assayed for each sample.

Figure 10 illustrates the correlation between fire-assay and PhotonAssay^{TM} measurements for two typical sample suites prepared from drill core and reverse circulation drilling materials respectively. In both cases, the PhotonAssay^{TM} measurements were performed on aliquots with a 2-3 mm top-size.

The correlation between the results obtained using the two analysis methods is very strong ($R^2 > 0.99$) for both drill-core and RC materials.

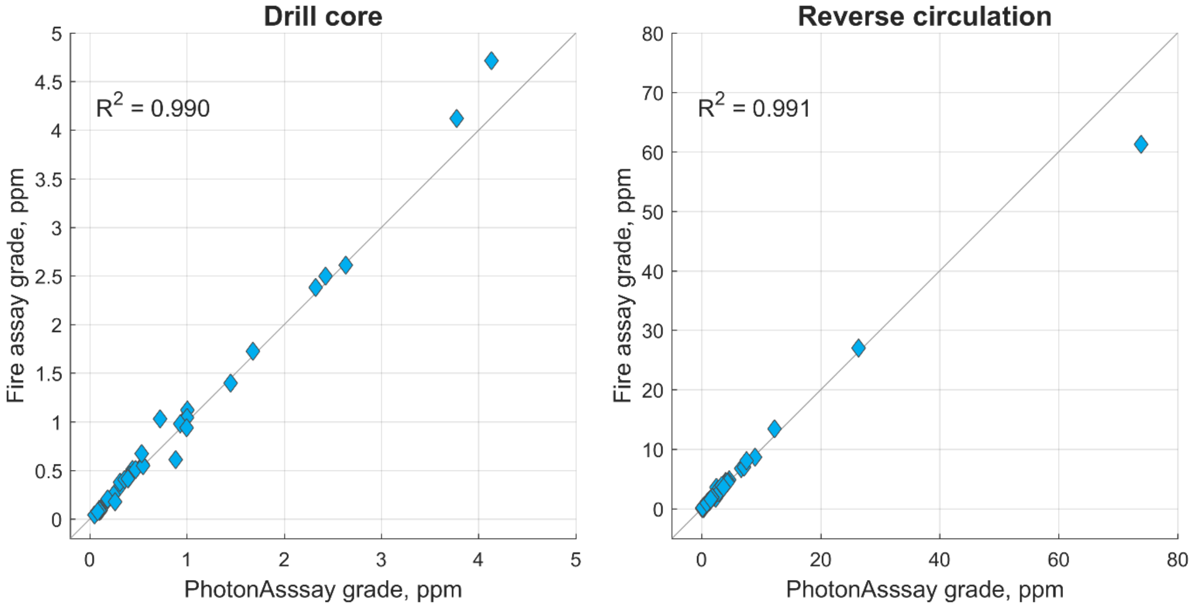

Figure 10. Fire-assay versus PhotonAssay^{TM} correlation plots for drill-core samples (left) and reverse circulation drilling samples (right). PhotonAssay^{TM} data are the average of measurements of two aliquots with a 2-3 mm top-size. Fire-assay data are the average of measurements of five aliquots.

Table 1 summarises the PhotonAssay^{TM} versus fire-assay grade correlations for the 10 drill sites from which samples were received. Two drill locations (labelled A and C in Table 1), showed statistically different and highly variable results for RAW and 15 mm top-size material. However, PhotonAssay^{TM} results obtained using 2-3 mm and 75 µm top-size material consistently showed very good agreement with fire-assay measurements.

Table 1. Correlations (adjusted R^2 values multiplied by 100) between fire-assay and PhotonAssay^{TM} gold grade measurements for sample suites obtained from 10 Australian drill sites.

Drill site*	**Sample Type****	**PhotonAssay^{TM} aliquot top-size**			
		RAW	**15 mm**	**2-3 mm**	**75 µm**
A	RC	79.4	81	97.8	96.7
B	RC	NR	NR	NR	99.1
C	DC	NR	13.1	85.1	98.9
D	Umpire	NR	NR	88.3	98.3
E	DC	NR	98.2	99.1	99.8
F	RC	97.8	98.6	98	99.2
G	RC	99.9	99.2	99.7	99.9
H	DC	NR	95.4	98.6	NR
I	DC	NR	NR	97.1	99.8
J	Umpire	NR	NR	82.4	NR

* Drill site codes are randomised throughout this report to maintain client anonymity.
**RC = Reverse Circulation drilling; DC = Drill Core; Umpire = 2-3 mm rejects from another laboratory.

Figure 11 provides an alternative presentation of the drill-core results shown in the left-hand plot in Figure 10, showing the distribution of measured grades obtained using PhotonAssay^{TM} on RAW, 15 mm, 2-3 mm and 75 µm top-size aliquots, and using fire-assay.

The results obtained using the different assay methods were subjected to two statistical tests: a conventional Student's t-test and a Tukey-Kramer test. Although more widely used, the Student's t-test makes assumptions about the data sets that may not be true in practice, including that data values are distributed normally and that the different analysis methods result in similar standard deviations. The Tukey-Kramer test does not require these assumptions to be met to be deemed valid. The results of both tests indicate that there are no statistically significant differences between the different assay methods.

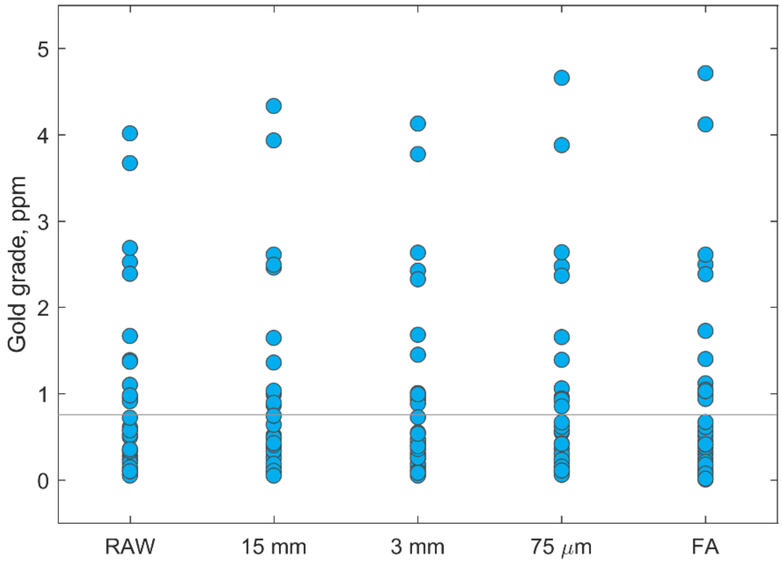

Figure 11. Distribution of gold grades measured via PhotonAssay™ on different size fractions (RAW, 15 mm, 3 mm and 75 micron) and via fire-assay on 75 micron material. The horizontal line indicates the mean grade.

Table 2 summarises the means and variances of the grade distributions for 4 RC and 4 DC Australian drill-sites, as determined via fire-assay and PhotonAssay™ performed on 2-3 mm top-size aliquots. Excellent agreement is observed, with no statistically significant differences found between assay results obtained using the two methods. In particular, comparison of the mean grades observed using the two techniques indicates that there is no systematic bias between the PhotonAssay™ and fire-assay results.

Evaluation of PhotonAssay™ and fire-assay repeatability

The results presented in the previous section demonstrate that the PhotonAssay™ method produces gold assay results that are in good agreement with those obtained using fire-assay. Further, the quality of the agreement improves as the particle size of the PhotonAssay™ samples is reduced.

Table 2. Means and variances of gold grade distributions measured via PhotonAssay^{TM} and fire-assay for 4 reverse circulation and 4 drill-core sample suites obtained from Australian drill sites.

Drill site*	**Sample Type****	Fire-assay (75 µm)			**PhotonAssay^{TM} (2-3 mm)**		
		N	**Mean**	**Variance**	**N**	**Mean**	**Variance**
A	RC	36	4.39	9.2	36	4.35	8.3
B	RC	75	2.99	15.8	75	3.02	15.4
C	RC	56	1.40	2.4	56	1.40	2.1
D	RC	35	6.60	158.0	35	6.72	176.6
E	DC	37	0.89	1.2	37	0.87	1.1
F	DC	81	3.04	55.7	81	3.18	78.3
G	DC	53	4.62	110.9	53	4.66	98.4
H	DC	20	3.97	14.9	20	3.84	14.1

* Drill site codes are randomised throughout this report to maintain client anonymity.
**RC = Reverse Circulation drilling; DC = Drill Core; Umpire = 2-3 mm rejects from another laboratory.

What this direct comparison of the two measurements cannot do is determine the source of any discrepancies, or in other words, determine separately the sampling and analysis errors for the two different assay methods.

Repeat measurements performed on the same sample provide one approach for estimating the size of these errors and their dependence on the sample preparation method. If multiple aliquots of material are independently prepared and separately measured, then comparison of the analysis results for these aliquots provides an estimate of the combined sampling plus instrumental errors.

For each drill-site sample suite, the root-mean square (RMS) of the relative standard-deviation in the measured gold grade is calculated for both fire-assay and PhotonAssay^{TM}; where PhotonAssay^{TM} data were collected at different particle sizes, then an RMS relative standard-deviation is determined for each. The relative standard-deviation is calculated as a percentage of measured grade. The RMS of the relative standard-deviation then provides an estimate of relative combined sampling + instrumental error for materials in the suite. Results are shown in Table 3 for sample suites from eight separate drill sites.

The columns report the RMS of the relative standard-deviations for PhotonAssay^{TM} measurements at 4 different particle sizes, and for standard 50 g fire-assay measurements. Samples with grades below 0.1 ppm have been excluded from the standard deviation and median calculations, as large errors for very low grade samples that are close to the instrument detection limit dominate the RMS calculation and mask the repeatability trend with particle size.

It should be noted that all of the fire-assay aliquots were drawn from the same bowl of pulverised ore. As such, variation between results for these aliquots captures the errors associated with sampling from the pulverised ore, but not 'up-stream' sampling errors resulting from the earlier crushing and splitting processes used to obtain a sample mass suitable for pulverisation. The reported fire-assay relative standard-deviation figures represent a lower limit on the total fire-assay repeatability.

Table 3. Average repeatability errors (sampling plus instrumental contributions) for sample suites collected from 8 Australian drill sites where PhotonAssay^{TM} measurements were performed using material with at least 2 different particle top-sizes. The root-mean square percentage relative standard deviation is shown for PhotonAssay^{TM} measurements with various aliquot particle top-sizes, and for fire-assay measurements (lower estimate, ignoring sampling errors during crushing and splitting). The number of original samples is shown in brackets.

Drill site*	**Median grade**	**PhotonAssay^{TM} RMS RSD**				**Fire-Assay RMS RSD**
		RAW	**15 mm**	**2-3 mm**	**75 µm**	**75 µm**
A	2.9 ppm	13%(37)	15%(37)	18%(59)	5%(37)	9%(59)
B	0.6 ppm	10%(34)	8%(34)	9%(34)	7%(35)	6%(35)
C	4.0 ppm	NR	45%(198)	21%(198)	12%(8)	14%(198)
D	3.3 ppm	NR	NR	7%(62)	NR	5%(80)
E	1.4 ppm	12%(56)	9%(55)	7%(56)	5%(56)	10%(56)
F	6.9 ppm	5%(5)	9%(35)	6%(35)	4%(33)	8%(35)
G	4.1 ppm	NR	31%(32)	17%(31)	NR	29%(32)
H	3.1 ppm	NR	NR	18%(40)	19%(39)	21%(41)

* Drill site codes are randomised throughout this report to maintain client anonymity.

Although the estimates of the RMS of the relative standard-deviations are themselves subject to statistical fluctuations, particularly for the drill-sites where relatively few samples were measured at a given particle size, the overall trend of the data is reasonably clear, with the PhotonAssay^{TM} measurement repeatability improving with reducing particle top-size.
The eight drill sites represent different operations with varying geology and gold distribution. Consequently, there is no systematic variation in repeatability with median gold grade.

For six of the eight drill-sites considered, the PhotonAssay^{TM} repeatability errors obtained using 500 g aliquots with a particle top-size of 2-3 mm are comparable to or better than the repeatability errors obtained using 50 g fire-assay aliquots. For drill-sites A and C, a significant improvement in repeatability is noticed when the aliquot top-size is reduced from 2-3 mm to 75 µm; for these materials, a reduction of the particle top-size to below 2-3 mm is likely to be required to achieve comparable sampling errors for PhotonAssay^{TM} and fire-assay.

A more detailed analysis of these data is presented in the appendix, where the decrease in repeatability error with particle top-size is studied in the framework of the Theory of Sampling.

Conclusions

Comparison grade measurements have been performed using PhotonAssay^{TM} and fire-assay on suites of materials received from Australian and international gold mining operations. Approximately 1500 aliquots were measured during factory testing of the first PhotonAssay^{TM} unit, and a further 10,000 sample aliquots were prepared and measured after installation at MinAnalytical Laboratory Services' site in Perth.

Excellent correlation is observed between measurements undertaken using the two assay methods, indicating that PhotonAssay™ generates analysis results that are consistent with those determined using the widely accepted fire-assay method.

A detailed study was undertaken to evaluate the effects of different sample preparation protocols. For most of the drill-sites studied, both reverse-circulation and drill-core materials can be adequately prepared by crushing the received material to a particle top-size of 2-3 mm and then sampling a PhotonAssay™ aliquot with a typical mass of 500 g. For two of the drill-sites, a further reduction in particle size is likely to be required to achieve sampling errors that match those of fire-assay using material pulverised to a top-size of 75 microns.

In conjunction with previously reported results comparing PhotonAssay™ and fire-assay on certified reference materials, we find that PhotonAssay™ is well-suited to the routine analysis of gold grades in drilling and process materials.

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Appendix - Sampling theory for gold ores

Introduction

Samples sent for analysis from gold mining or processing operations represent only a tiny fraction of the bulk material. Similarly, the samples received by the assay laboratory – typically weighing several kilograms – must be reduced to an analytical aliquot suitable for the chemical analysis method being used.

We focus exclusively on the second stage of the sampling process, namely the drawing of the analytical aliquot from bulk samples received at an assay laboratory. The methods used for in-field sampling of the original bulk material are out-of-scope for this report.

The sampling process used to draw the analytical aliquot should meet two requirements:

- It should be *unbiased*, meaning that on average, the composition of the aliquot should match the composition of the bulk sample; and
- It should be *low variance*, meaning that the variation in the composition of the aliquot about the expected mean should be a low as can be reasonably achieved.

The principles by which unbiased sampling should be performed are well established. As gold-bearing and barren mineral phases may differ in their physical properties such as density, hardness, particle-size etc, the methods and equipment used to reduce the sample volume should not depend on these parameters.

The random variation in the composition of the aliquot can be parameterised in terms of the standard deviation, σ, of the distribution of compositions that would be obtained if a large number of aliquots were drawn and measured. It is often more convenient to work in terms of the variance, defined as the square of the standard deviation.

The fundamental sampling equation (Gy (1973) and Gy (1982)) states that the variance, v, associated with drawing an aliquot of mass M_L from a sample of mass M_S with gold grade a is given by the following formula:

$$\frac{v}{a^2} = \left(\frac{\sigma}{a}\right)^2 = k_s\left(\frac{1}{M_L} - \frac{1}{M_S}\right) \qquad (1)$$

Here k_s is the sampling constant that depends primarily on the distribution of the masses of gold particles in the material being sampled.

For finely disseminated gold comprising many small particles, k_s is small (Figure 12, top). In the limit that the gold is uniformly distributed throughout the sample, $k_s \to 0$ and any aliquot is completely representative of the bulk sample. Conversely, when gold is present as a small number of large nuggets, k_s is large and the random variability in aliquot composition will be high (Figure 12, bottom). The sampling constant k_s, which has units of mass, can be thought of approximately as the mass of sample that on average contains one typically-sized gold particle.

In practical cases, the aliquot mass M_L is generally much smaller than the bulk sample mass M_S. The sampling variance then varies inversely with the aliquot mass. As the aliquot mass becomes larger, the sampling variance reduces further; in the limit that the entire sample is used as the analytical aliquot ($M_S = M_L$), the variance is trivially zero.

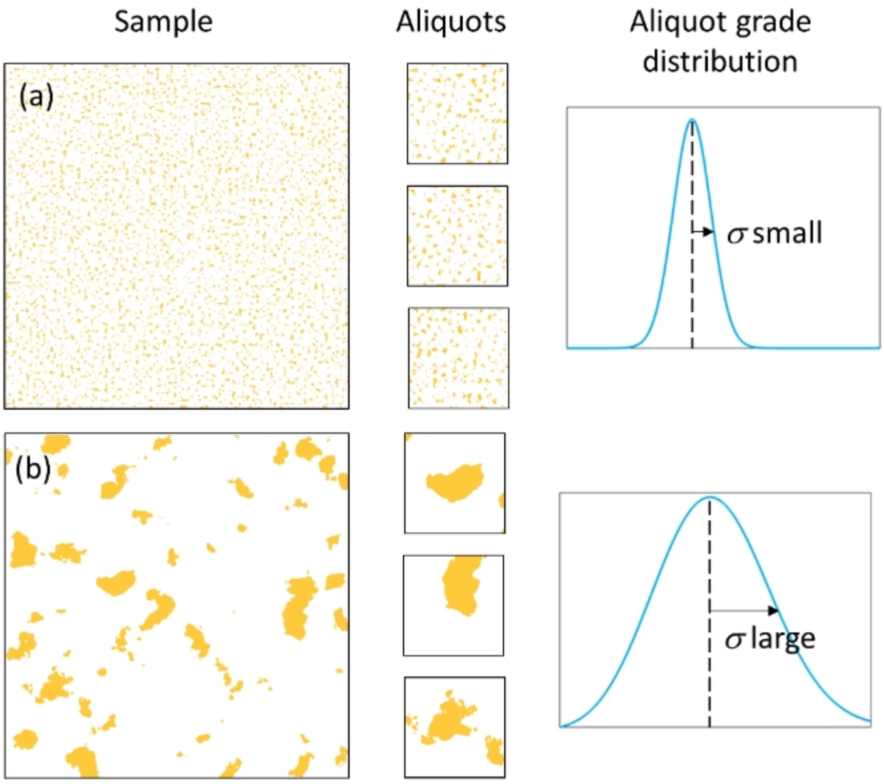

Figure 12. Illustration of drawing of aliquots from samples with finely disseminated gold (a) and coarse gold (b). The resulting distributions in sampled aliquot gold grade are shown on the right.

Figure 13 plots the change in standard deviation of the aliquot sampling distribution as a function of aliquot mass for a sample mass of 6 kg. The standard deviation is arbitrarily normalised to unity at an aliquot mass of 50 g.

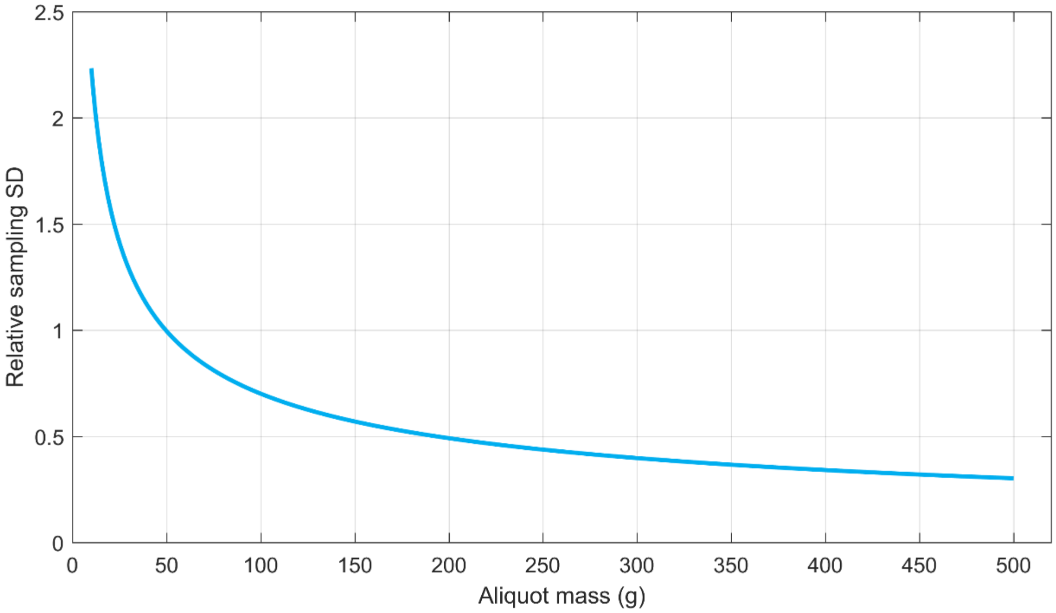

Figure 13. Variation in standard deviation of sampled aliquot grade distribution as a function of aliquot mass.

Figure 13 shows that increasing the aliquot mass from 50 g (typical for fire-assay) to 500 g (typical for PhotonAssay^{TM}) reduces the sampling error *for a given material* by more than a factor of 3, with the relative standard deviation reducing from 1.0 to 0.30. This calculation assumes that the same sample preparation method is used for both PhotonAssay$^{\text{TM}}$ and fire-assay.

Impact of particle size reduction

Samples received at the assay laboratory from mines or exploration programs are usually unsuitable for direct sampling for fire-assay. The material may be in the form of a drill core, or have too large a particle size for convenient reduction to an aliquot of 50 g. If the gold in the samples is coarse, or agglomerated into veins or other structures, the sampling constant k_s may also be too large for sampling with reasonable variance.

To overcome these challenges, the material is usually passed through one or more size reduction steps. The aim of these steps is to reduce the overall material particle size to facilitate sub-sampling, and hopefully to reduce the sampling constant by reducing the gold particle size. Typically for fire-assay aliquot preparation, the material may be:

- Coarsely crushed to a particle size of approximately 15 mm.
- Finely crushed to a particle size of 95% passing 2-3 mm, and then sub-sampled down to a mass of about 3 kg.
- Pulverised to 85% passing 75 μm, before the final 50 g aliquot is drawn.

The question of how the sampling constant k_s varies with different forms of sample preparation – and in particular, with the reduction in the material top-size – is complex and subject to considerable debate. Pierre Gy, widely recognised as one of the founders of sampling theory, described sampling as “A random process liable to introduce errors such as in chemical analysis.” (Gy, 1979).

Gy’s Theory of Sampling provides an estimate of the sampling constant for a given material when correct sampling processes are followed, viz:

$$k_s = fglcd^3 \tag{2}$$

where f is the particle shape factor (typical value of 0.5)

g is the size-range or granularity factor (typically taken to be 0.25 for raw and 15 mm top-size material, 0.5 for 2-3 mm top-size, and 0.75 for pulverised material)

l is the liberation factor

c is the mineralogical composition factor, approximately given by the metal density (19.3gcm^{-3} for gold) divided by the sample grade (for example 10^{-6} for a 1 ppm sample)

d is the typical particle size

All of the parameters appearing on the right-hand size of equation (2) depend on the masses, compositions and size-density distributions of particles being sampled, and hence are intrinsic properties of the sampled material.

A naïve interpretation of equation (2) would suggest that the sampling constant decreases like the cube of the particle diameter, and so reducing the sample top-size from 2-3 mm to 75 μm should significantly improve the sampling process.

However, as discussed in François-Bongarçon & Gy (2002), the liberation factor is itself a significant function of particle size. The factor varies over the range 0-1 and describes whether the process used to reduce the bulk material particle size is also capable of ‘liberating’ or separating gold particles from their gangue. When the material top-size is large compared to the ‘liberation distance’ or typical distance between gold particles, reducing the top-size has relatively little effect on the sampling constant. However, at smaller material top-sizes, reducing the particle size tends to separate gold particles from one another and reduces the sampling constant.

Various models for the liberation factor have been proposed (see for example Gy (1982)); here we adopt the simple empirical model of François-Bongarçon (1992) and write

$$l = \left(\frac{d_l}{d}\right)^b \tag{3}$$

where d_l (the liberation distance) and b are empirical parameters to be determined

Combining equations (1), (2) and (3), we obtain

$$\frac{v}{a^2} = \left(\frac{\sigma}{a}\right)^2 = K\left(\frac{1}{M_L} - \frac{1}{M_S}\right)d^\alpha \tag{4}$$

where K is a single constant that incorporates contributions from f, g, c and d_l and $\alpha = 3 - b$ captures the variation in sampling error with material top-size. An experimental program is then needed to find the values of K and α for a given deposit.

To this end, we follow the sampling tree method described by Minnitt et al. (2007). This involves testing replicate aliquots with different top-sizes to determine their gold grade, inferring the variance as a function of top-size and then fitting the results to determine the two parameter values. Ideally, large samples are split and analysed in a series of steps, starting with as-received material, and then proceeding down through top-sizes of 15 mm, 2-3 mm and 75 μm. The fitted K and α values can then be used to determine the fundamental sampling error for any arbitrary top-size for a given mineral deposit, or alternatively to find the sample or aliquot mass required to achieve a given sampling precision.

Even though this method is typically used to derive the masses of required for initial at-mine sampling, it can also be utilised to determine errors associated with sampling when applying different laboratory assay techniques. Lyman (2016) suggests sampling theory can provide information all the way down to the size of a typical laboratory aliquot.

Application to larger samples

The potential for measuring larger samples than the standard 50 g fire-assay aliquot has been explored previously. For example, Lyman (2016) presents results for samples from two different deposits; he finds that reducing the particle top-size down to 2-3 mm reduces the sampling constant from about 40 g for the as-received material to approximately 1-2 g. For a 500 g aliquot, this would lead to a sampling error (1 SD) of about 4-6% relative.

Based on these findings, Lyman suggests a ‘pulverise and leach’ process, where 1 kg samples are simultaneously pulverised and leached by rotating them in a special mill, together with leaching solution and grinding media. The leach solution is analysed using flame atomic absorption spectrometry (FAAS) and any unleached gold remaining in the solid phase can be analysed via conventional fire-assay.

The process of cyanide leach (or gold cyanidation) was first developed in 1783, is well understood and provides a robust method for extracting gold. However, cyanide salts are extremely toxic and the pulverise and leach process produces significant waste. It also requires a two-step process - leach followed by fire-assay - to obtain a quantitative estimate of the total gold content.

The PhotonAssay™ method provides an alternative approach for measuring large aliquots that avoids these difficulties.

Analysis of PhotonAssay™ sampling errors in the Theory of Sampling framework

To further understand the dependence of sampling errors on the sample preparation method, a more detailed study was conducted using four of the ten suites of samples received from different drill sites in Western Australia, New South Wales and South Australia.

For the PhotonAssay™ samples the relative standard deviation (RSD) in the measured gold grade was calculated for each pair of duplicate samples taken at different particle top-sizes with a mean grade above 0.5 ppm. A correction was made for the estimated instrument error, which varies as a function of gold grade. The root-mean square value of the corrected RSD results was then calculated for each particle size and sample suite. These data provide an estimate of the sampling error as a function of particle top-size and aliquot mass.

Following the procedure described by Minnitt & Assibey-Bonsu (2010), we can divide equation 4 by the mass term and take logarithms to obtain:

$$\ln\left(\frac{M\cdot v}{a^2}\right) = \ln K + \alpha \ln d \qquad (5)$$

Consequently, a plot of $y = \frac{M\cdot v}{a^2}$ versus $x = \ln d$ where $M = \left(\frac{1}{M_L} - \frac{1}{M_S}\right)^{-1}$ should result in a straight-line graph with a slope of α and a y-axis intercept of $\ln K$, allowing the values of these parameters to be straightforwardly determined.

Figure 14 plots the results for drill-site A (36 samples). The reduction in the variance with particle size is modest, with a slope of α = 0.6. The inferred sampling error calculated from equation (5) for a typical PhotonAssay™ 500 g aliquot with a 2-3 mm top-size is approximately 12%; the corresponding error for a fire-assay 50 g aliquot with a 75 μm top-size is 14%.

The exercise was repeated for the other three participating drill-sites in the sample-tree study. Table 4 summarises the results obtained.

Table 4. Results of fits of log(mass-weighted variance) versus log(particle size) for four sample suites. The inferred sampling error (1 standard deviation) for typical PhotonAssay™ samples (500 g, 2-3 mm top-size) and typical fire-assay samples (50 g, 75 mm top-size) are also shown.

Drill-site*	α	K	PhotonAssay sampling error (500 g)	Fire-assay sampling error (50 g)
A	0.6	14	12%	14%
B	0.8	2.7	5%	4%
C	0.6	5.7	7%	7%
D	0.7	3.6	6%	5%

* Drill site codes are randomised throughout this report to maintain client anonymity.

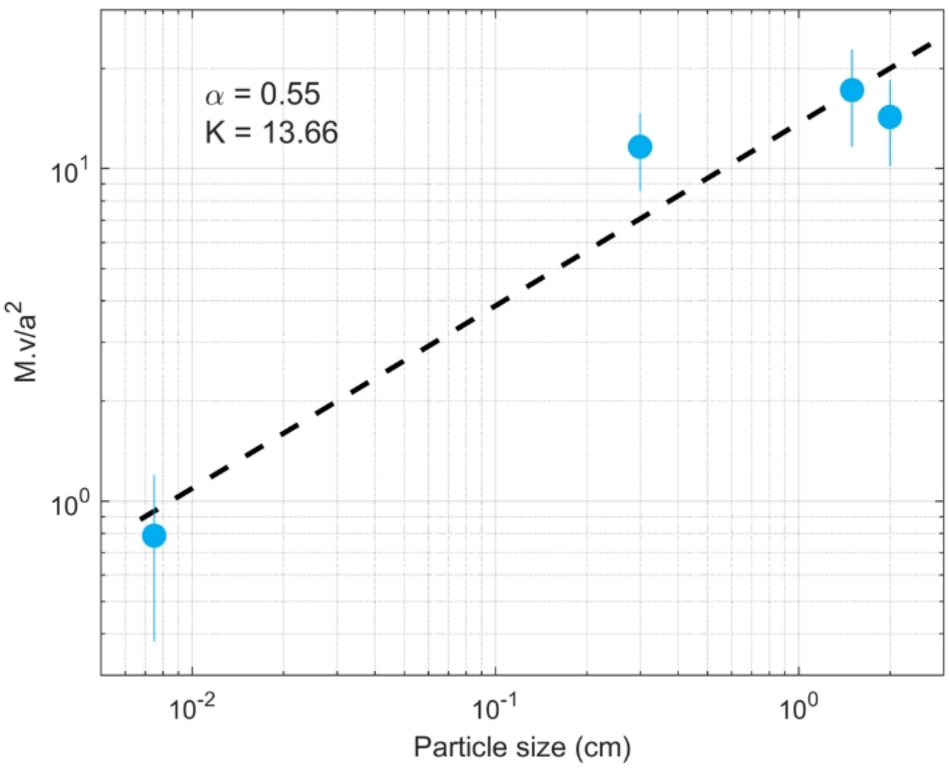

Figure 14. Plot of mass-scaled relative variance versus particle size on log-log scales. The sampling parameters α and K are determined from the slope and d = 1 cm intercept of the best-fit line (dashed).

In each case, the reduction in sample error with particle size is small, with α values in the range 0.6-0.8. Consequently, sampling errors for 500 g PhotonAssay™ aliquots taken at a 2-3 mm particle size are generally similar to those obtained using 50 g fire-assay aliquots with a 75 µm top-size.