Crushed reference materials and potential bias during sample preparation of gold ore

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Abstract

Drill samples extracted from the field for submission to a laboratory are a resource mining company's most valuable asset. A key part of the resource estimation process is validation of laboratory results through a quality control program that encompasses the entire field to data workflow. Implements currently available to the market, particularly for gold and base metal projects, largely consist of pulverised reference materials, supplied in sachets, and submitted 'blind' to the laboratory for analysis. However, sample preparation is a critical part of the laboratory process, and pulverised reference materials are not involved in this step. As part of reporting requirements, the JORC (2012) code and N43-101 requires assessment of the nature, quality and appropriateness of the sample preparation methods to be detailed.

Crushed iron ore and bauxite reference materials have been utilised as part of sample preparation assessment for many years. However, crushed reference materials for gold ores have not been available due to high nugget effect, resulting in significant between sample variance obscuring other biases. In order to assess the potential for biases and errors in sample preparation prior to the analysis of gold concentration by fire assay, a crushed reference material (CRM) containing homogeneously distributed gold was engineered.

A multi-laboratory round-robin exercise to assess the effect of sample preparation on the accuracy and precision of the overall laboratory process was then conducted. Initial results indicate that sample preparation processes can systematically bias gold grades. Further investigations are required to assess the laboratory and material-specific drivers to the observed biases, and under which circumstances the use of a homogeneous CRM may be justified as part of the quality assurance scheme of mining grade control and resource estimation programs.

Keywords: Quality control, standards, sample preparation, sampling, crushed reference material, laboratory analysis, fire assay, photon assay.

Introduction

One of the most valuable assets for mining and exploration companies are the samples extracted from drilling programmes for the purposes of targeting or resource estimation. Drill samples provide the mining and exploration company with quantifiable data for the purposes of elemental concentration estimations, and their spatial distribution within the ore or potential ore body. Drill samples are submitted to a laboratory for analysis. Regardless of the type of drilling being performed, the physical properties and mass of the submitted drilling samples need to undergo sample preparation at the laboratory prior to analysis. Sample preparation usually entails multiple processes of particle size reduction, mass reduction via sub-sampling, and final analysis aliquot collection. Submitted drill

samples may have particle sizes up to 20 mm, or in metre lengths in the case of core, and masses up to 10 kg. Aliquots for analysis generally are up to 50 g for gold analysis, and as low as <1 g for some acid digests with the particle size being typically <100 µm. The most important outcome when designing a sample preparation protocol is to ensure the final aliquot for analysis is representative of the original sample or interval submitted.

As such, it is critical for the mining company to independently assess the sample preparation process due to the high potential for systematic or random biases, sampling and preparation errors, particularly in the case of high nugget value gold ores (Abzalov, 2016; Dominy, 2016, amongst others). In practice, however, the mining company focussing on the assessment of biases that could occur in the analytical stage which are usually minor compared to sample preparation. It is well understood that the systematic biases in analysis are usually minor compared to the random variance in sample preparation processes, which in turn is minor compared to the random variance in field collection stage (Stanley and Smee, 2007).

This paper is particularly concerned about the potential for systematic biases to occur in sample preparation, and the methods and materials available to adequately assess the sampling errors. The study of systematic bias in sample preparation for high nugget ores is confounded by the high variability between field duplicate samples of natural gold ores. Field duplicates are a common method currently used to assess sample preparation errors. The investigation of systematic bias in the preparation of samples from high nugget ores is obscured by the high variability of field duplicate samples of natural gold ores. For instance, a duplicate field sub-sample sent to a secondary laboratory often exhibits field sub-sample variability as the greatest component of the sum of variability derived from the sampling, preparation, and analysis process. This obscures investigation of systematic sample preparation and analytical bias between laboratories unless in large sample population investigations.

Considering conventional reference materials submitted to the laboratory for the purposes of QAQC (assessment of precision and accuracy) are pulverised and analysis-ready, the mining and exploration company is left with few options to adequately assess sample preparation biases. The manufacture of a certified reference material with large particles (>3 mm) having sufficiently low between sample variance has not been comprehensively studied within the industry. The development of a product with sufficiently low between sample variance would enable an assessment of quality control in sample preparation process such as crushing, splitting and pulverising to be made. This study investigates, in particular, the potential for systematic biases to occur in sample preparation for which a pulverised crushed reference material (CRM) is unable to assess. In order to evaluate a sample preparation bias, the CRM were prepared and analysed at multiple laboratories followed by a comparison to a secondary analysis of the prepared CRM at an alternate single laboratory. The investigation was undertaken during the certification of a CRM certified for gold. Furthermore, the emergence of assay methods in the gold space that make use of a crushed sample, and high sample masses, necessitates some consideration for the use of a corresponding CRM with similar physical characteristics as the samples being analysed. While the development of a CRM for quality control of both the sample preparation and fire assay analytical systems is the primary focus of the paper, the usefulness of the CRM for quality control of photon assay is not lost, and some comparisons are also made between the two methods (sample preparation-fire assay, and photon assay).

QAQC Practices in the minerals industry

Quality assurance (QA) and quality control (QC) systems are largely universally understood within the modern minerals industry, and their application is summarised by Abzalov (2016). While the design of the quality assurance program will be specific to the mining or exploration context, it commonly involves the use of strategies that are designed to assess accuracy and precision, along with risk of sample-to-sample contamination. As such, QAQC programs include the use of blanks, duplicate sub-

samples and submitted certified reference materials. The frequency of insertion is determined by the QA system. Duplicate sub-sampling with sample collection and preparation processes can include field duplicates, crush-split duplicates and repeat aliquots from the pulverisation stage. A QA program may also include the submission of samples prepared at a primary laboratory, to a second laboratory for check analysis.

Of all of these strategies at play, the use of a pulverised CRM is the primary method for which a quality assessment of accuracy or systemic bias can be made. Duplicates, regardless of the stage within the analytical process, provide a means to assess precision at the point in the process the duplicate is made, and include contributions to precision from all remaining steps along the analytical chain. Within the laboratory, a crush-split is a common strategy taken after size reduction and provides two separate pulverisation sub-samples for analysis. Post-pulverisation splits can be taken by either a duplicate pulverised sub-sample, or a second analytical aliquot taken from a single pulverisation sub-sample.

Conventional certified reference materials are dry powders which require no further particle size reduction or sample preparation and are ready for analysis by digestion. They are ideally homogeneous at the final aliquot scale relative to the analytical precision. These pulverised CRMs are manufactured by dedicated companies with expertise in processing and homogenisation of materials and are available across almost all mineral groups.

In the case of photon assay, however the use of pulverised CRMs in an analytical method preferring a crushed sample has been problematic (Dominy *et.al.*, 2024). The inconsistent performance of pulverised CRMs in photon assay over repeat measurements have been noted due to the unstable characteristics of finely pulverised materials in the assay jars used.

Crushed CRM use in iron ore and bauxite commodities

For the assessment of bias and contamination in sample preparation within bulk commodity industries such as iron ore and bauxite, crushed certified reference materials have been standard practice for many years. Other industry terms for crushed CRM include *coarse ore standards*, *geostandards*, and *RC-chip CRM.*
Crushed certified reference materials offer advantages over pulverised certified reference materials such as:
- the 'blindness' of the CRM is enhanced as it has a similar appearance to routine samples
- the CRM can assess precision and accuracy for both sample preparation and analysis
- the replacement of a blank (say a silicate material) for a material with similar chemistry as submitted samples provides a more realistic assessment of contamination and carry-over without the risk of contamination and therefore loss of data from the routine samples themselves.
- as part of a comprehensive QA system which includes pulverised CRMs, an assessment of contribution of sample preparation to analytical bias and precision.

An example of the utility of crushed CRMs in an iron ore context has been demonstrated by Carter and Armstrong (2023). In this case study a sample preparation equipment malfunction caused a systematic bias that would not have been able to be detected except for the use of a crushed CRM. In the case of iron ore and bauxite crushed CRMs are manufactured using natural ores from the mine and homogenised and packaged to appear as a reverse circulation drill sample. Crushed CRMs are typically natural ores crushed to less than 3 mm to 5 mm, and typically packaged in 2 kg to 4 kg units. The CRMs are certified in a similar way to pulverised CRMs; by a network of competent laboratories with multiple units submitted for sample preparation and analysis. Homogeneity and characterisation studies are generally followed according to ISO 17034 (2017) and Guide 35 (2017).

During the certification process, the laboratory prepares the entire sample and does not take any aliquots from the CRM submitted in its submitted form, as might be the case for a pulverised CRM. Standard sample preparation practices should be followed to produce a final aliquot for analysis. The consumption of the entire sample or unit in sample preparation is important, as each sample contains a certain level of within-unit heterogeneity. In this way the crushed CRM mimics a real sample. Samples often contain a chemical bias by particle size, depending on mineralogy. In the case of iron ore materials, the fines are typically elevated in SiO_2 and Al_2O_3 (IM Standards unpublished data). The same principles are well documented with gold enrichment in the fine portion of samples (Carswell and Sutton, 2014; Minnitt *et al*, 2011; Reid, 2014). In order to produce an unbiased final aliquot for analysis, size reduction, and sub-sampling of heterogeneous samples in the laboratory needs to follow good sampling practices to ensure the final result is representative of the original sample collected from the field.

Following the statistical treatment of data received from the participating laboratories, certified values and their respective uncertainties are determined. Hence the certified values and uncertainty estimates of the crushed CRM incorporate the contribution of sample preparation.

Crushed CRMs can be routinely manufactured to achieve similar between-unit variance to pulverised CRMs for major and minor analytes (Carter and Armstrong 2023). This is important as the crushed CRM must have sufficiently low between-unit variance in relation to analytical precision for effective detection of possible sample preparation biases.

Certified reference materials can only contribute to a quality outcome for the part of the laboratory to which they are exposed and used. A crushed CRM would allow the assessment of quality for the entire sample preparation and analysis process to be made, whereas pulverised CRMs bypass the sample preparation process and only assess quality for analysis (Figure 1). In this study the photon assay sample preparation methodology is not employed, with delivered samples requiring no further particle size reduction or sub-sampling.

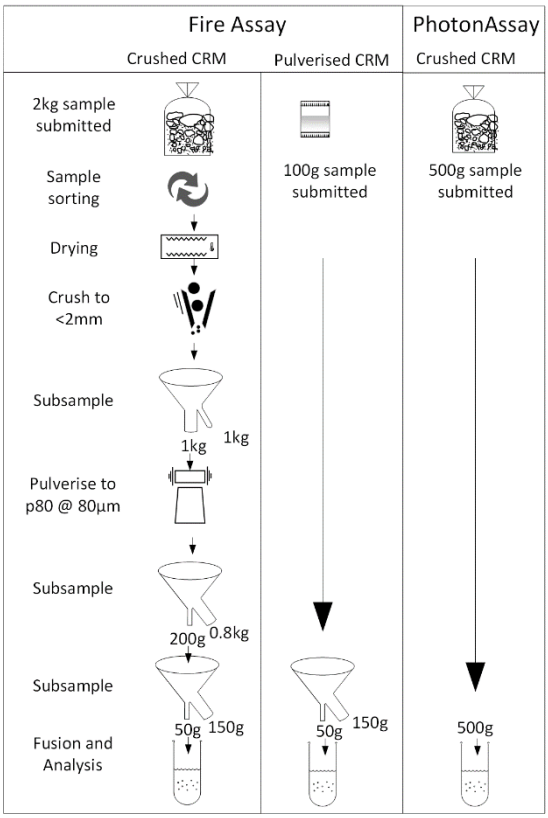

Figure 1. Generalised sample preparation process of certified reference materials used in this study in fire-assay and photon assay.

Production and certification of a crushed gold CRM

Despite the standardised use of crushed CRMs for bulk ores, they have not been commonly manufactured for other commodities such as gold or base metals. Crushed CRMs have not been available for gold ores due to the nugget effect with significance between and within unit variances in the samples obscuring other biases.

IM standards developed a patent-pending production process that results in a crushed gold CRM engineered by dispersing gold within a crushed mineralogical structure. The crushed CRM is manufactured to appear as a gold-bearing reverse-circulation ore sample with a particle size of less than 3 mm and packaged into both 0.5 kg and 2 kg units.

The production process techniques were similar to those used for bulk ore crushed CRMs, ensuring minimum between unit variance was achieved, while maintaining an appropriate level of within-unit heterogeneity. The manufactured crushed CRM is internally heterogenous, with both mineralised and non-mineralised particles present across the particle size range. The fines portion demonstrates a bias towards the mineralised particles, to reflect typical natural ores, and is therefore sensitive to sample preparation sub-sampling processes.

The certification of the crushed gold CRM followed two independent studies, homogeneity analysis and characterisation analysis. In order to analyse each CRM sample, the crushed CRM needs to be prepared in the laboratory for analysis. As such, each of these studies includes a full assessment of the

contribution to variance from sample preparation, in addition to the analytical component normally assessed by a pulverised CRM.

Homogeneity Study

Multiple (15) 2 kg units selected systematically throughout the production process were extracted and sent to a single laboratory for analysis under repeatability conditions. The samples were randomised before being submitted to the laboratory to assess if any trends found were due to manufacturing or analysis. The laboratory prepared the samples by pulverisation in an LM5 mill followed by the extraction of three separate sub-samples. A 25 g aliquot was then extracted from each sub-sample and analysed by Pb-collection fire assay, with an ICP finish. A total of 45 results were returned for statistical assessment by ANOVA at the 5% significance level. A p value = 0.23 was obtained indicating the material can be considered homogeneous, with the between-unit variance less than the within-unit variance when analysed by Pb-collection fire assay.

Characterisation Studies

The characterisation study followed the homogeneity study via a network of competent ISO 17025 accredited laboratories for Pb-collection fire assay. Multiple 2 kg samples were systematically selected throughout the batch then randomly assigned to each laboratory for single analysis per sample. The participating laboratories were based in Australia and Canada, and included both major international laboratory groups in addition to smaller independent laboratories. Sample preparation was via a crushing and sub-sampling step, followed by either a LM2 or LM5 pulverisation step. The sample

preparation method used was contingent upon the laboratory equipment available, and their routine procedures typically used for customers in their region. The analysis was conducted by Pb-collection fire assay with either an AAS or ICP finish.

Characterisation study for photon analysis was also undertaken by submission of multiple 0.5 kg samples at multiple laboratories. No sample preparation was required with supplied samples becoming the final aliquot after decanting into analysis jars. Each 0.5 kg lot manufactured was analysed in its entirety.

The analytical results from 11 fire assay and seven photon assay laboratories were returned from the characterisation study. Each laboratory received five samples for analysis. The results of the certification process are shown in Table 1.

Table 1. IMS-237 Certificate summary, with certified value, assigned uncertainties, and characterisation study details. FA=sample preparation plus Pb-collection fire assay, PA= photon assay

Method	Analyte	Unit	Certified Value ($\hat{y}$)	Standard Deviation (s)		95% Confidence Interval (CI)		u_{CRM}^	k#	U_{CRM}~	No. of Labs (ISO/IEC 17025)	No. Samples
				1 SD	1 SD Within Lab	lower	upper					
FA	Au	g/t	2.06	0.123	0.068	1.99	2.14	0.066	2	0.13	11	55
PA	Au	g/t	2.07	0.077	0.072	2.03	2.11	0.069	2.36	0.16	7	35

Results of IMS-237 characterisation by photon assay

The results in Table 1 show agreement in gold concentration between sample preparation Pb-collection fire assay and photon assay. For photon assay the samples did not undertake particle size reduction or sub-sampling prior to analysis. Of significance is the broad agreement in concentration values amongst the participating laboratories as shown in Figure 2. The results are shown by way of a box and whisker plot for gold concentration in grams per tonne. The size of the box is representative of the first and third quartile from the within-lab distribution, the horizontal line is the median, and the vertical lines extend to the minimum and maximum of the five sample results. Figure 2 shows results between the laboratories distributed around the mean.

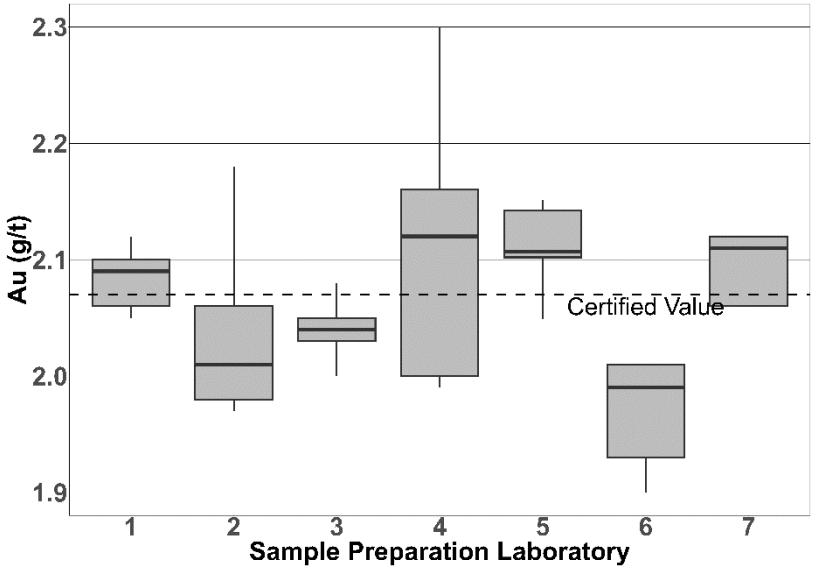

Figure 2. Box and Whisker plot of IMS-237 characterisation study from multiple 0.5 kg samples submitted to seven laboratories for PhotonAssay analysis only, with no prior sample preparation.

It is notable from Table 1 that the global standard deviation for photon assay is significantly lower compared to sample preparation - fire assay. The within-laboratory standard deviation is similar for both analytical techniques.

Results of IMS-237 characterisation by sample preparation and fire assay

In order to determine the source and significance of the higher global standard deviation in the fire assay characterisation study, a similarly detailed presentation of the results is shown in Figure 3.

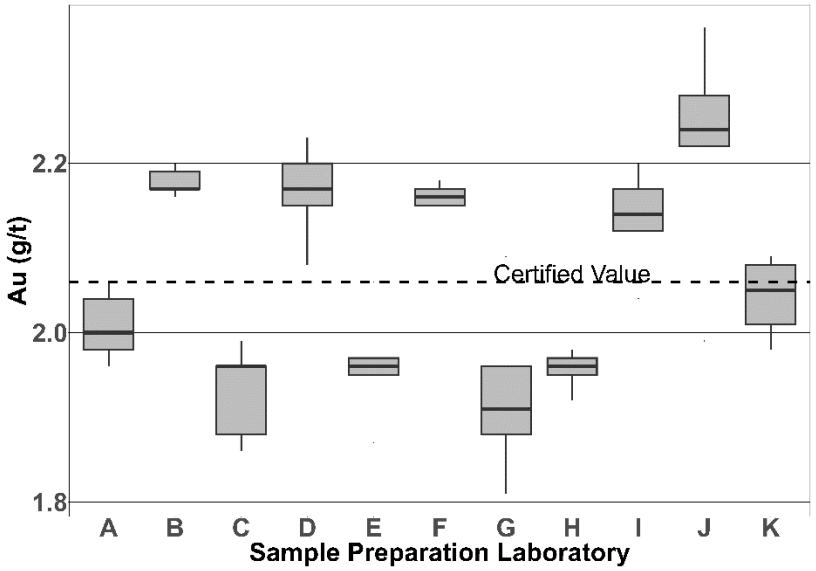

Figure 2. Box and Whisker plot of IMS-237 characterisation study from multiple 2 kg samples submitted to 11 laboratories for sample preparation and fire assay analysis.

With the potential exception of laboratory K, the characterisation data in Figure 3 is distributed broadly bimodal by grade. The global range of results is from -7% to +9% of the median grade. Some of the

laboratories are clearly biasing higher than the certified value (2.06g/t), and others on the low side. The total range of 16% gold concentration is significant when compared to the within-laboratory variance shown by all of the box plots by laboratory identifier. As each laboratory passed the CRM through both sample preparation, and analysis, it is difficult to determine where the bias in the data originates. Internal laboratory quality control CRMs, when reported with the results, were checked for compliance with no issues identified. Internal CRMs, however, will only assess the analytical component of the overall laboratory process. Similarly, a pulverised CRM submitted for single analysis with the candidate samples were reviewed against their certified concentrations and uncertainties, with no outlier values reported. There is potential, therefore for the biases to occur in sample preparation. An investigation through an umpire analysis program was therefore performed.

Umpire Analysis

In order to investigate and resolve the trends in the fire assay data observed, and by following what would be a standard practice within the industry, analysed CRM samples from the fire assay study were recovered from a number of the certifying laboratories for umpire analysis at a single laboratory. In the case of photon assay, no further umpire analysis was performed.

Pulverised samples from laboratories B and D (bias high) and laboratories E and H (bias low) were recovered and reassigned new sample identification. The samples were then submitted to laboratory H for fire assay.

The results are shown in Figure 4. The original analysis for each of the laboratories (B, D, E and H) are shown (box 1) alongside the re-analysis performed at laboratory H and prepared at laboratories B, D and E respectively. Laboratory H conducted fire assay analysis at both 25 g (box 2) and 50 g (box 3) aliquot size to test for incomplete digestion caused by reagent consumption.

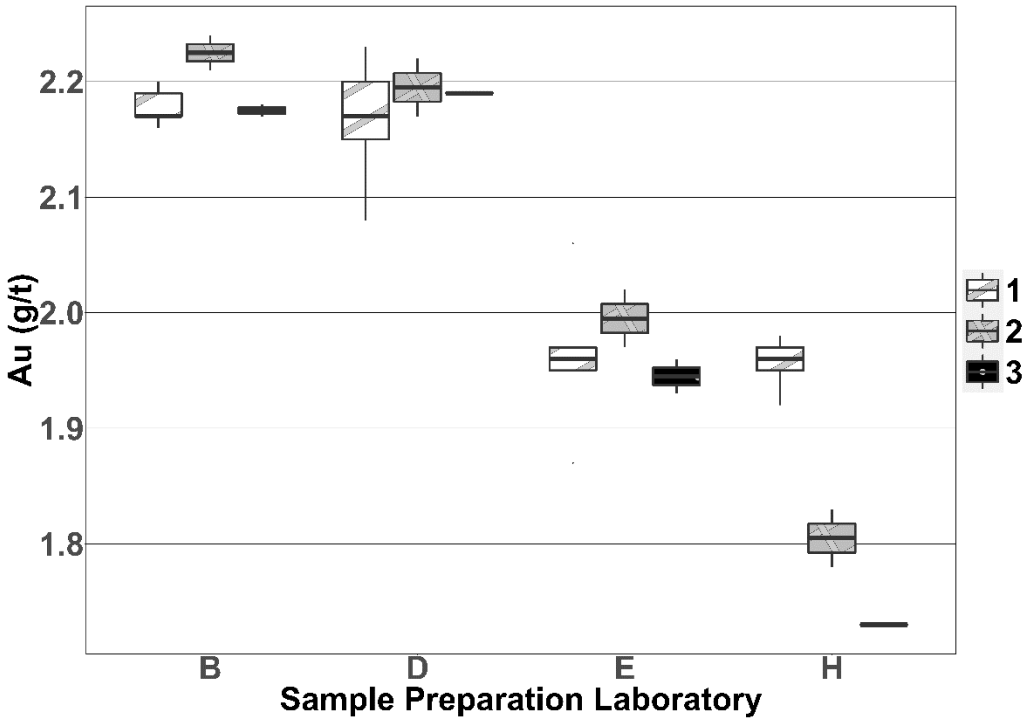

Figure 4. Replicate analysis of samples pulverised at laboratories B, D, E and H during characterisation study. Replicate analysis performed at laboratory H shown alongside the original analysis (1), using 25 g (2) and 50 g (3) aliquots.

Figure 4 shows that replicate fire assay analysis at laboratory H largely aligns with the original results from the primary laboratory where the samples were prepared. The original analysis was confirmed in all cases (laboratory B, D and E). If the bias originated from analysis, then the umpire results from laboratory H would be expected to align with the original results from laboratory H. Interpretation of the data leads to the conclusion that a sample preparation bias has occurred. It should be noted the certification process, and subsequent umpire analysis does not suggest there is a consistent bias over time, or across multiple submissions at each of these laboratories.

While at this stage no further work has been conducted to identify the source of the bias, it is clear the engineered reference material is behaving in such a way that there is the potential for the detection of a systematic bias within sample preparation. The homogeneity study demonstrated the material has an effective level of homogeneity, when analysed by one laboratory, but the nuances in sample preparation processes between laboratories seems to be causing a positive or negative bias from the certified mean.

In addition to the gross trends, there is a noticeable but smaller bias between the fire assay for a 25 g aliquot and 50 g aliquot suggesting that at 50 g, the samples were not completely digested in the process resulting in a slightly low bias.

Conclusions and further work

This study has identified an industry-wide issue in routine QAQC programs for the submission of field and drill samples to laboratories for sample preparation followed by analysis. Traditional certified reference materials are pulverised and the submitting geologist remains exposed to biases in sample preparation that may currently be undetected. Sample preparation processes include mass and particle size reduction mechanisms with opportunity for sampling variances to occur affecting the quality of the analysis. There is potential for the industry to make use of a certified reference material that could be submitted by the geologist and determine the contribution of sample preparation to uncertainty budgets.

While crushed CRMs have been utilised in bulk ore commodities for many years, the development and efficacy of a crushed CRM containing a certified amount of gold has been elusive to the industry until now. The reference material manufactured demonstrated a fit for purpose level of gold homogeneity making it suitable for submission as a QAQC sample at the sample preparation stage of the laboratory process, thus providing information on the contribution sample preparation makes to the overall laboratory data variances.

Furthermore, the between laboratory observations and subsequent umpire analysis suggests the scale of a systematic bias occurring in sample preparation is significant in relation to the analytical precision of the fire assay method. Additional work to assess the specific sample preparation and material drivers are required, including a longitudinal study to test if laboratories maintain a consistent sample preparation bias on gold grades over time.

The sample preparation processes for photon assay route were not tested in this study, with participating laboratories providing final aliquots which required no sub-sampling or crushing prior to analysis in its crushed form. Provision of 2 kg sample units for crushing and sub-sampling prior to photon assay is required in order to directly compare bias between the different sample preparation methodologies at multiple laboratories. Regardless, the manufacture of a crushed CRM for photon assay has applications for establishing more robust quality control methods for this, and other methods, that make use of a crushed sample for analysis.

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A geologist with over 20 years' experience in the precious and base metals mining industry, with experience across exploration and underground mining, resources estimation, and geo-metallurgy for complex ore deposits. As a director at Independent Mineral Standards, developed proprietary procedures and technology for producing homogeneous coarse certified reference materials (CRM) which rival traditional pulverised CRM for analyte variance.