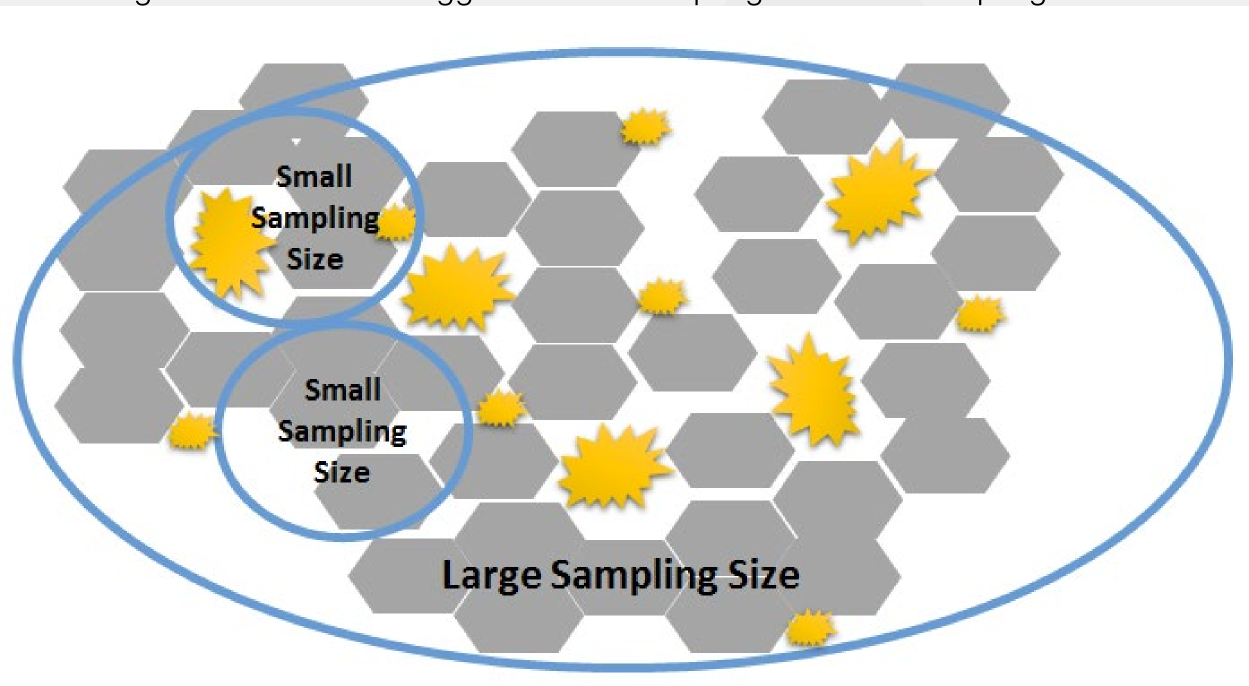
Achieving homogeneity in CRMs from 'nuggety' high grade gold ores

By Craig Hamlyn 27th August, 2018

Traditional milling methods (e.g. LM2 Bowl and disc pulveriser) are ineffective at reducing the grain size of gold particles. The highly malleable nature of gold simply results in the smearing of gold on hard surfaces, the formation of gold leaf that form into 'cigar' shapes and back again into gold leaf. This issue has led to the widespread belief that only synthetic materials or gold ores containing fine grained and homogenously distributed mineralisation can be used to make Certified Reference Materials (CRM's). Ore Research & Exploration Pty Ltd's (ORE) proprietary processing technology is a game changer. ORE provides quality assurance on the homogeneity of all CRM's produced, regardless of the nature of source materials, including 'nuggety' gold ores. Furthermore, ORE's proprietary processing technology does not involve any compositional change to the ore other than grain size reduction. Unlike practices employed by some other producers, there is no removal of coarse gold particles by sieving or any addition of fine-grained 'gold minerals'. OREAS CRM's are entirely sourced from naturally occurring ore deposits of various mineralisation styles and when appropriate, blended with geologically matching waste rock to achieve target grades.

Figure 1. The Gold Nugget Effect - Sampling Size and Sampling Error.



A fit for purpose CRM is one certified for the analyte(s) and grade of interest by an analytical method similar to the one being monitored in a QC setting. Ideally, the mineralisation style and matrix should also be similar in order to obtain a similar response to fusion/digestion. Pulp CRM's should be immune to segregation and be stable within their packaging.[1] Often overlooked is the importance of the required level of homogenisation of the CRM. There should be minimal, ideally negligible, contribution of sampling error from the CRM. This means the CRM itself should not be the cause of analytical bias seen in results due to heterogeneous particle size and disbursement of gold.

[1]ORE's proprietary processing technology overcomes segregation issues in the packaged CRM so there is no need for homogenisation (eg. bottle-rolling) prior to subsampling for analysis. Sulphide-bearing CRMs are packaged under inert gas to prevent oxidation.

The homogeneity of the CRM should be quantified at the intended sample mass to be assayed at the laboratory. For example, the sampling error of a gold CRM should be quantified for a typical 30g fire assay charge weight. This allows users to know what the potential contribution of sampling error originating from the CRM could be to the overall error seen in assay data. The Certificates for all OREAS gold CRMs contain this information in the Statistical Analysis section. For example, OREAS 61f is described as having a *"1RSD of 0.252% calculated for a 30g fire assay or aqua regia sample"*.

Figure 1 above shows an abstract microscopic view of pulverised gold ore. A small sample size could chance upon a nugget or could miss entirely. Larger sample masses are obviously more likely to improve representation and lower sampling errors. Of critical importance to any consumer of CRMs (with gold CRMs in particular given their ppb and ppm levels of concentration) is the minimum sample size required to obtain a negligible sampling error (e.g. <1% RSD). The level of homogeneity (expressed as a per cent relative standard deviation) at a typical 30g fire assay sample weight can be calculated using the sampling constant (Ingamells and Switzer, 1973). The ORE reduced subsample method utilises this relationship between standard deviation and sample mass. By substantially reducing the sample mass to be assayed, a sampling error is induced. In this approach the sample aliquot is substantially reduced to a point where most of the variability in replicate assays should be due to inhomogeneity of the reference material. Measurement error becomes negligible in comparison to sampling error.

All gold reference materials prepared by ORE undergo this reduced subsample method by using instrumental neutron activation analysis (INAA) at Actlabs in Ancaster, Canada or ANSTO in Lucas Heights, Australia. INAA is a highly precise non-destructive technique compared with conventional fire assay. INAA can be used on samples as little as a gram or fraction of a gram. By assaying a reduced subsample a sampling error is theoretically induced and this enables the absolute homogeneity of the CRM to be quantified.

Ingamells and Switzer in their 1973 paper described a method for determining the sampling constant:

$$\text{Sampling Constant (Ks)} = \text{RSD}^2 \times \text{mass}$$

(Ks is the required mass to achieve a 1% RSD). E.g. If the RSD across 20 x 1g INAA determinations is 4%, Ks = 4g

The RSD at any sample weight can be calculated accordingly:

$$\text{Eg. RSD at 30g} = \sqrt{\frac{RSD_{INAA}^2 \times m_{INAA}}{30}}$$

The effectiveness of ORE's proprietary processing technology can be demonstrated by the two case studies following. These show the repeatability of gold in samples from a 'nuggety' source where the material is prepared by traditional comminution methods (achieving an above average laboratory specification of >95% passing 75 microns). The materials are then further processed by ORE's proprietary processing technology and then compared to conventional methods. A third case study examines ORE's CRM database and plots the homogeneity of all gold CRMs produced since 2011.

Case study 1

In this study, the 'nuggety' gold source is the MMG Ltd's Golden Grove VMS deposit in Western Australia. A 2 tonne batch of high grade Cu ore was prepared and following homogenisation, six samples were taken and assayed with up to 3 repeats per sample (see Table 1 below). The data ranged 0.37 to 5.45ppm Au with a mean of 1.3ppm. Clearly Au is not homogenous within sample repeats nor between the six samples (extreme outliers shown in red below).

Table 1. Gold repeatability in high grade Cu ore prepared by traditional comminution methods to achieve >95% passing 75 microns.

Sample#	Au ppm FA25/AA	Au-Rp1 ppm FA25/AA	Au-Rp2 ppm FA25/AA	Au-Rp3 ppm FA25/AA
1	1.26	2.76	**4.07**	1.16
2	2.26	0.96	**5.45**	
3	1.23	1.11	1.10	
4	0.98	0.80	**0.49**	
5	0.72	**0.37**	1.09	
6	0.72	1.0	0.73	

FA25/AA = 25g fire assay charge with AAS

A 5 tonne batch of high grade Zn ore was also prepared to >95% passing 75 microns. Following homogenisation, the material was emptied into twenty-eight drums. A 100g sample was taken from every odd numbered drum creating fourteen separate samples. These samples were dispatched for gold analysis to Intertek Genalysis, Perth for 25g gold fire assay in triplicate. Table 2 below shows the results with a raw average of 2.62ppm Au. The variability is very high with a standard deviation of 3.5ppm and there is evidence of gold micro-nuggets with results up to 17.88ppm.

The source materials were then further processed by ORE's proprietary processing technology and blended in appropriate proportions to create five new OREAS CRM's at various grades of Cu, Zn, Au, etc. Following homogenisation, twenty 10g subsamples of each RM were taken at predetermined intervals across the entire batch. The 10g subsamples were dispatched to Actlabs in Ancaster, Canada for high precision instrumental neutron activation analysis (INAA) on 1g sample weights. This method was chosen to demonstrate homogeneity because it has minimal measurement error. The analysis can be employed using small subsamples thereby inducing a sampling error in the RM. Any heterogeneity and/or 'nugget effect' will be greatly magnified at a 1g sample weight compared to a 25-50g fire assay charge weight.

Table 2. Gold repeatability in high grade Zn ore prepared by traditional comminution methods to achieve >95% passing 75 microns.

Sample#	Au ppm FA25/AA	Au-Rp1 ppm FA25/AA	Au-Rp2 ppm FA25/AA
1	1.57	0.77	0.92
2	1.09	1.75	2.9
3	1.62	2.88	**17.88**
4	2.04	2.1	1.46
5	2.16	**4.72**	2.29
6	2.57	1.79	1.67
7	**5.5**	0.97	1.07
8	1.65	1.57	0.62
9	1.7	**6.6**	1.79
10	1.04	1.16	0.81
11	1.2	1.26	0.78
12	1.23	0.93	0.72
13	1.43	4.23	**16.02**
14	2.99	0.67	1.95

FA25/AA = 25g fire assay charge with AAS

Table 3. Gold repeatability at the 1g level in CRM's prepared by ORE's proprietary comminution technology.

Sample#	OREAS 620	OREAS 621	OREAS 622	OREAS 623	OREAS 624
	ppm	ppm	ppm	ppm	ppm
	INAA	INAA	INAA	INAA	INAA
1	0.739	1.26	1.89	0.829	1.18
2	0.684	1.26	1.91	0.836	1.11
3	0.701	1.26	1.86	0.866	1.12
4	0.685	1.31	1.83	0.828	1.19
5	0.681	1.29	1.85	0.873	1.14
6	0.684	1.26	1.86	0.866	1.12
7	0.700	1.26	1.85	0.853	1.18
8	0.696	1.29	1.82	0.846	1.20
9	0.659	1.27	1.81	0.796	1.07
10	0.659	1.26	1.86	0.822	1.11
11	0.688	1.33	1.78	0.813	1.09
12	0.709	1.33	1.81	0.838	1.09
13	0.694	1.29	1.84	0.802	1.10
14	0.686	1.26	1.84	0.846	1.09
15	0.707	1.20	1.82	0.838	1.09
16	0.658	1.27	1.89	0.852	1.08
17	0.694	1.24	1.86	0.874	1.18
18	0.676	1.27	1.87	0.857	1.08
19	0.652	1.26	1.86	0.842	1.06
20	0.705	1.28	1.93	0.84	1.32
Mean	0.688	1.273	1.852	0.841	1.13
SD	0.021	0.03	0.036	0.022	0.062
RSD^{1g}	3.03%	2.32%	1.94%	2.59%	5.52%
RSD^{30g}	0.56%	0.43%	0.36%	0.48%	1.02%

The INAA results are shown in Table 3 above where RSD^{1g} shows the Relative Standard Deviation across the 20 x 1g samples. RSD^{30g} provides the equivalent Relative Standard Deviation at a nominal 30g fire assay charge weight using the Sampling Constant (which utilises the known relationship between standard deviation and sample mass; see Ingamells & Switzer, 1973).

The RSD^{30g} data confirms the high levels of gold homogeneity achieved. The homogeneity is of a level such that ***sampling error is negligible*** for a conventional 30g fire assay (or aqua regia) determination. This allows users to unequivocally attribute error seen in assay data to the laboratory, with negligible contribution from the CRM.

Case study 2

In this study, the 'nuggety' gold source is Doray's Andy Well deposit in Western Australia. A 23-tonne parcel of primary high-grade gold ore was supplied by Doray as (nominal) minus 20mm coarse aggregate. The material was transferred into steel drums loaded on to twenty-six pallets. A 1kg sample was taken from one of the drums from each pallet to yield 26 samples in total. Each sample was pulverised to an above average laboratory preparation specification of >95% passing 75 microns and homogenised prior to subsampling to 115g. The 26 x 115g samples were then dispatched to Intertek Genalysis in Perth, Australia for Au analysis in duplicate (Dup). Results are shown in Table 4 below.

The duplicate data in Table 4 confirm the presence of micro-nuggets. Only Pallets 20 and 22 show good repeatability. The others show levels of heterogeneity from slight (Pallets 2-6, 9, 12-16, 19, 23 and 25) to extreme (Pallets 1, 7-8, 10-11, 17, 18, 21, 24 and 26).

Again, as for Case Study 1, the material was further processed by our proprietary processing technology and blended in appropriate proportions to create three gold ore CRM's ranging between 3-7ppm Au.

Following homogenisation, twenty 10g subsamples of each CRM were taken at predetermined set intervals in order to be representative of the entire ~4 tonne batches. The 10g subsamples were dispatched to Actlabs in Ancaster, Canada for high precision instrumental neutron activation analysis (INAA) on 85mg subsample weights. The INAA results are shown in Table 5 where RSD^{85mg} shows Relative Standard Deviation across 20 x 85mg samples and RSD^{30g} provides the equivalent Relative Standard Deviation at a nominal 30g fire assay charge weight using the Sampling Constant (Ingamells & Switzer, 1973).

The RSD^{30g} data confirms the very high levels of gold homogeneity achieved. Once again, the homogeneity is of a level such that ***sampling error is negligible*** for a conventional 30g fire assay (or aqua regia) determination.

Table 4. Gold repeatability in Andy Well gold ore prepared by traditional comminution methods to achieve >95% passing 75 microns.

SAMPLE	Au ppm
Pallet 1 of 26	4.93
Dup	10.79
Pallet 2 of 26	6.51
Dup	7.7
Pallet 3 of 26	7.73
Dup	8.33
Pallet 4 of 26	5.45
Dup	6.23
Pallet 5 of 26	5.22
Dup	3.95
Pallet 6 of 26	3.27
Dup	3.74
Pallet 7 of 26	10.9
Dup	5.84
Pallet 8 of 26	12.87
Dup	5.42
Pallet 9 of 26	8.85
Dup	8.09
Pallet 10 of 26	15.24
Dup	8.53
Pallet 11 of 26	4.76
Dup	10.13
Pallet 12 of 26	9
Dup	9.65
Pallet 13 of 26	11.9
Dup	10.23
Pallet 14 of 26	8.15
Dup	6.9

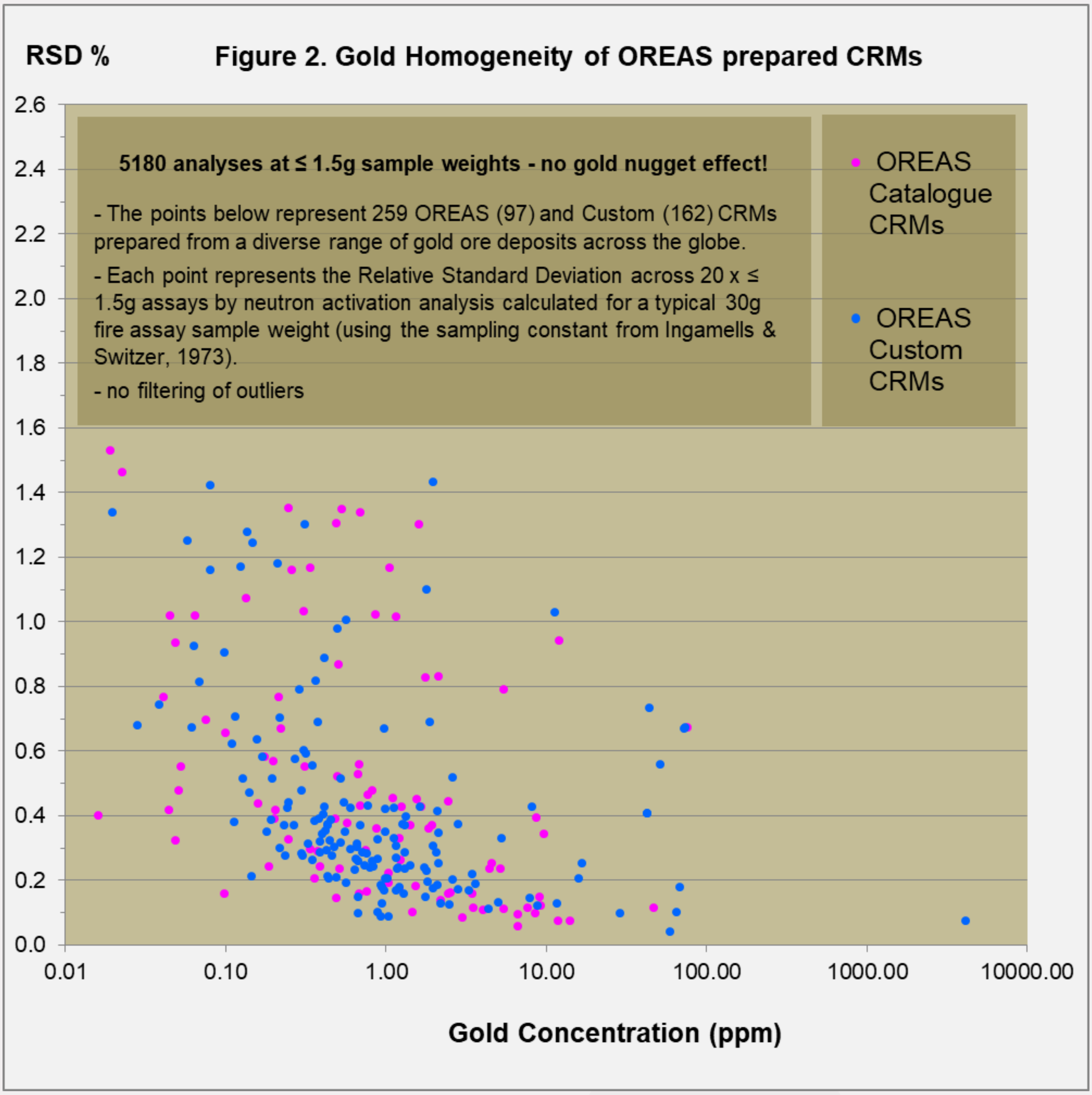
SAMPLE	Au ppm
Pallet 15 of 26	5.9
Dup	3.93
Pallet 16 of 26	5.66
Dup	6.72
Pallet 17 of 26	10.29
Dup	5.3
Pallet 18 of 26	11.24
Dup	8.41
Pallet 19 of 26	2.66
Dup	3.72
Pallet 20 of 26	4.43
Dup	4.4
Pallet 21 of 26	12.15
Dup	9.2
Pallet 22 of 26	7.75
Dup	7.45
Pallet 23 of 26	9.77
Dup	7.3
Pallet 24 of 26	8.3
Dup	13.01
Pallet 25 of 26	4.05
Dup	3.05
Pallet 26 of 26	14.56
Dup	8.48
MEAN	7.65
SD	3.07

Table 5. Gold repeatability at the 85mg level in gold ore CRM's prepared by ORE's proprietary processing technology.

Sample#	OREAS 214	OREAS 215	OREAS 216
	ppm	ppm	ppm
	INAA	INAA	INAA
1	3.11	3.63	6.84
2	3.05	3.70	6.81
3	3.13	3.58	6.69
4	3.09	3.57	6.60
5	3.12	3.55	6.82
6	3.12	3.53	6.82
7	3.13	3.71	6.93
8	3.04	3.80	6.81
9	3.03	3.69	6.83
10	2.99	3.72	6.81
11	3.06	3.75	6.78
12	3.04	3.65	6.73
13	3.11	3.62	6.89
14	3.04	3.66	6.74
15	3.15	3.63	6.79
16	3.07	3.70	6.73
17	3.18	3.72	6.79
18	3.04	3.66	6.85
19	3.04	3.51	6.84
20	3.09	3.58	6.78
Mean	3.08	3.65	6.79
SD	0.049	0.078	0.072
RSD^{85mg}	1.58%	2.13%	1.06%
RSD^{30g}	0.08%	0.11%	0.06%

Case study 3

In this study, ORE's entire database of INAA results accumulated over the period 2011-2018, is plotted for every gold-bearing CRM produced. This data includes CRM's developed for the OREAS range (97) and Custom CRM's (162) developed specifically for clients from client-supplied materials. Figure 2 depicts the OREAS catalogue CRMs in red and Custom CRMs (produced from client-supplied material) in blue. Each point represents the Relative Standard Deviation (RSD) of the 20 x ~1g INAA determinations calculated for a typical 30g fire assay charge weight using the Sampling Constant (as discussed above). The graph below shows a predominance of data in the 0.1-0.6% RSD range and with all data below 1.5% RSD. Towards the lower level of detection (below 0.1ppm or 100ppb) the RSD range is higher 0.5-1.5% pointing towards an increase in precision errors due to limitations of measurement. There does not appear to be any relationship between RSD and CRM type (i.e. Custom CRM's are equally as homogeneous as OREAS CRM's).



References

Ingamells, C. O. and Switzer, P. (1973), Talanta 20, 547-568.