

Homogeneity Assessment of Crushed and Pulverised Iron Ore Certified Reference Materials. Implications for Laboratory Quality Control.

J Carter¹ and B J Armstrong²

1. General Manager, Independent Mineral Standards, Bayswater, WA, 6053. Email: john@imstandards.com.au

2. Operations Manager, Independent Mineral Standards, Bayswater, WA, 6053. Email: bruce@imstandards.com.au

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ABSTRACT

Best practice for the submission of samples to an internal or commercial laboratory requires quality control materials to be included for the purpose of independently and comprehensively assessing laboratory performance. These quality controls include the use of certified reference materials (CRMs) and may be blind to the laboratory. Iron ore companies purchase these materials from reputable manufacturers from stock of run of mine materials at the appropriate grades. The international standard, ISO17034, specifies the competency requirements for organisations manufacturing reference materials, and includes rigorous requirements for the assessment of homogeneity, stability and establishment of property values and their uncertainties. Homogeneity is one of the most important measures of suitability for all certified reference materials and refers to the degree to which the composition and properties of a sample are uniform throughout the batch, relative to the analytical precision of the method. More specifically, homogeneity studies of candidate reference materials should be assessed for both within sample variance, and between sample variance with appropriate statistical controls. The design and application of homogeneity studies are discussed as they apply to both crushed and pulverised reference materials.

Crushed certified reference materials have been utilised by the iron ore industry for a number of years and provide the user with a critical assessment of variances in sample preparation in addition to analysis. Crushed reference materials are similar in presentation to an RC sample, and are generally used as discrete parcels of material submitted to the laboratory from the field. Pulverised certified reference materials miss the sample preparation step and are subsampled from the delivered sachet at the point of analysis. This paper compares the relative homogeneity performance of crushed and pulverised certified reference materials by grade across key iron ore chemical constituents. Outcomes are benchmarked to the international standard ISO9516 for the determination of various elements in iron ores by lithium borate fusion and X-ray fluorescence. Practical implications are discussed with reference to a case study from an iron ore laboratory in the Pilbara.

Keywords: Crushed, Pulverised, Certified Reference Material, Quality Control, Homogeneity.

INTRODUCTION

Iron ore companies conducting exploration, strategic or tactical mine planning, collect samples from the field and submit them to in-house or commercial laboratories for analysis. In order to obtain confidence in the results from the contract laboratory and assess their performance, the mining company needs to implement a quality assurance regime throughout the custody chain from sample collection to analytical stage. Part of this quality assurance (QA) regime typically includes insertion of duplicate samples and reference materials into the sample stream submitted to the laboratory for analysis alongside the regular drill samples (Abzalov, 2016, Sterk, 2015). The analytical results of these quality control samples are regularly monitored and benchmarked. Quality control through the use of reference materials is therefore fundamental to exploration and mine planning activities and are a critical activity for establishing confidence and reliability of the estimations made.

The submission of a certified reference material (CRM) is the primary tool for the assessment of accuracy and bias in analytical results. Purchased from a reputable supplier, CRMs are a stable material, sufficiently homogenised and characterised by a metrologically traceable procedure (ISO17034, 2016). The CRM is accompanied by a certificate containing consensus values, their associated uncertainties, and a statement of metrological traceability. Uncertainties can be used to establish control limits that are monitored by the exploration companies throughout the drilling program. These CRMs are ideally “blind” to the laboratory and may have been sourced from the exploration company’s ore or manufactured from appropriate material. The CRMs from the field are usually submitted in the calico bags that would normally contain a field sample.

Within the iron ore mining industry, there are two types of CRMs used; pulverised and crushed. Pulverised iron ore CRMs are sourced from natural ores and are usually milled and size screened to p95 of 54 µm, followed by homogenisation prior to packaging in typically 10 g units for submission to the laboratory along with the drill samples. The pulverised CRM represent a dilemma for the laboratory as they are separated from the drill samples as they undergo drying, particle size reduction, and sub-sampling before being reintroduced prior to the final sub-sampling to typically 0.5 g for creation of the fused bead from which the XRF analysis is performed. The obvious difference in visual presentation between drill sample and a pulverised CRM allows identification by the laboratory of CRM samples, which may be flagged as client CRM and placed at the end of analytical sequences.

Crushed CRMs are also manufactured from natural ores which have been dried, crushed and screened to typically p95 of 3 mm or 5 mm followed by homogenisation and packaging into 2 kg to 4 kg units. Crushed CRMs when submitted are similar to an RC drill sample with similar visual presentation, mass, and particle size. The samples undergo identical sample preparation processes as submitted field samples such as sorting, drying, crushing, pulverising with typically two sub-sampling steps in the process prior to presentation for analysis. The laboratory should not be able to identify and separate the crushed CRM from the field samples within the laboratory workflow, nor allocate it to a different analytical sequence to the field samples.

The difference between the processing of a pulverised and crushed CRM within the laboratory is significant as illustrated in Figure 1. While both CRMs assess the quality of the analytical steps, the crushed CRM also includes variance contributions from the sample preparation process. Sample preparation includes various manual or automated handling steps where sampling errors due to particle size reduction and/or mass reduction can and does occur (Gy, 1982). While visibility of the additional contribution to quality of the final result through sample preparation is important with a crushed CRM, one of the key components being assessed arises due to the differences in homogeneity between crushed and pulverised CRMs.

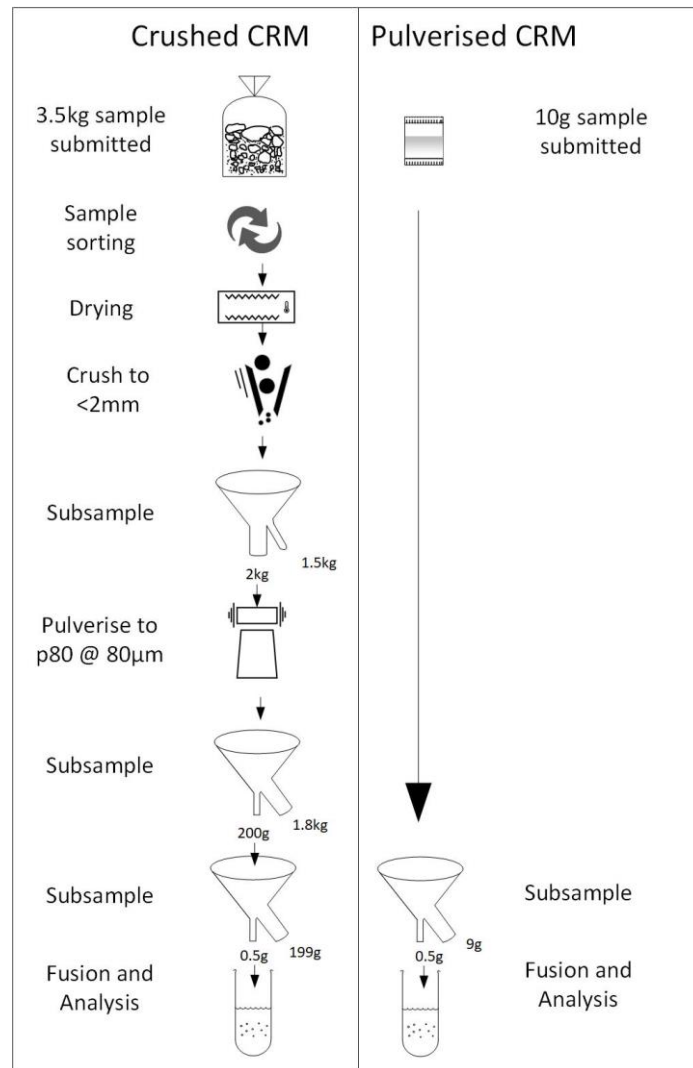


FIG 1 – Process of Crushed and Pulverised CRMs within the laboratory workflow.

While it is critical CRMs are homogeneous between sample units, the significant difference between crushed and pulverised CRM is the internal heterogeneity within the sample. This comes about because a crushed CRM includes a wide range of particle sizes. Pulverised CRMs are nominally <54 µm and are subsampled during analysis. Crushed CRMs include particles from <5 µm to 5 mm, with batch specific particle size distributions and are analysed in their entirety.

The propensity for particle size segregation during transport, transfer, and storage occurs by a number of mechanisms such as percolation and rolling and is widely described (Levy and Kalman, 2001). The freely segregating material of heterogenous samples requires good laboratory practice in sub-sampling and materials handling to obtain a final pulverised sample for analysis that is representative of the original submitted sample. It is important to point out that the potential for sample heterogeneity to cause erroneous results are the same for field samples as they are for crushed CRMs, hence why this is an important addition to the overall quality control plan.

Good laboratory sub-sampling practice is vital because the mineral concentrations of crushed iron ore are not consistent by particle size. The degree of mineral concentration by particle size varies between iron-ores, typically with relatively lower Fe concentrations in finer products, and corresponding elevated SiO₂ and Al₂O₃ concentrations in the finer products as shown in Figure 2.

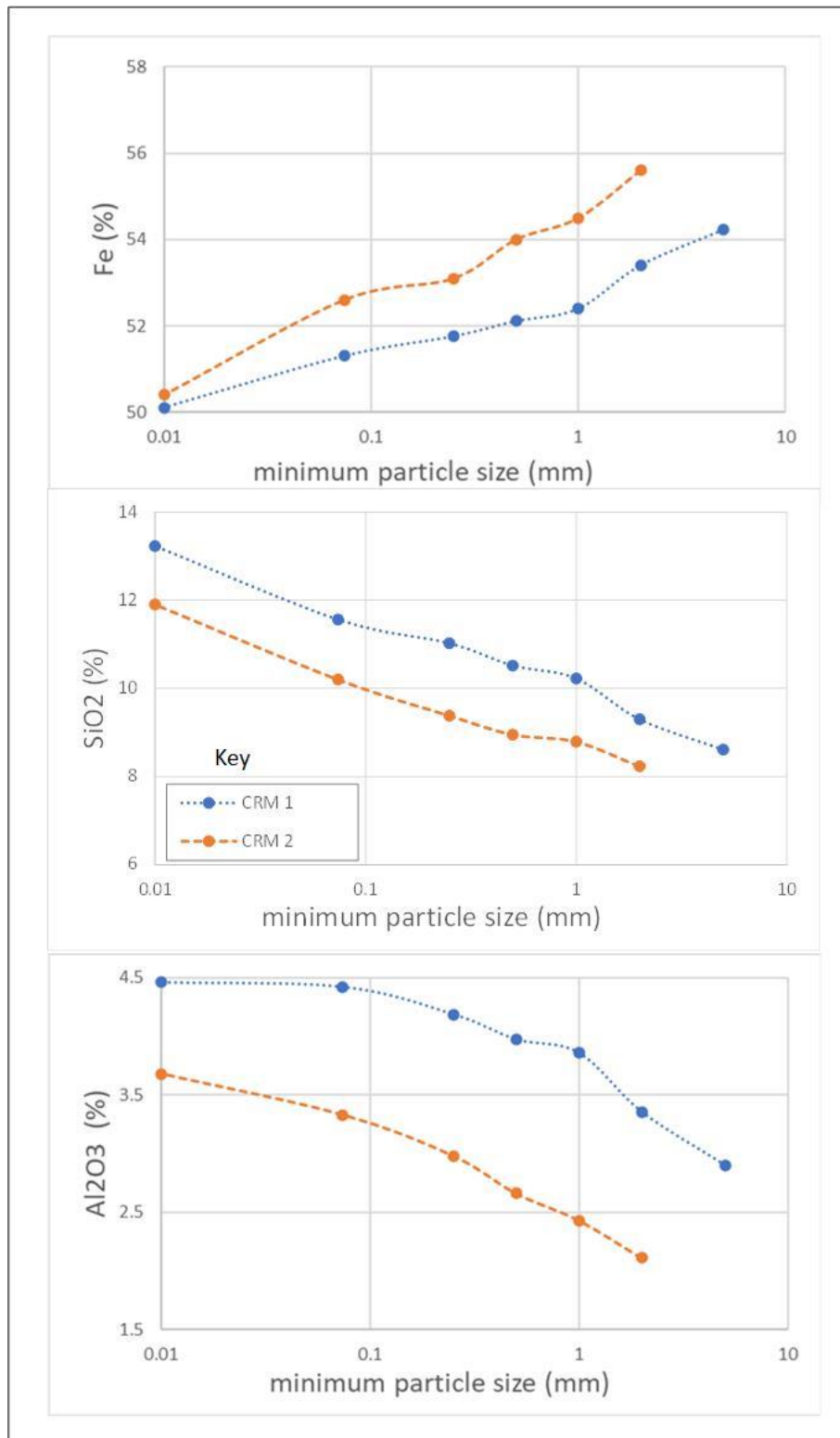


FIG 2 – Fe, SiO₂ and Al₂O₃ concentrate of two crushed CRMs by particle size.

The data in Figure 2 was derived by bench screen tests of stacked sieves of decreasing mesh openings across a 2 kg bag randomly selected from two different crushed CRM batches manufactured from iron ores sourced from the Pilbara. The heterogeneity of the CRM by particle size trends in a consistent way between each CRM analysed.

MANUFACTURE AND CERTIFICATION OF REFERENCE MATERIALS

The manufacture and certification of CRMs are guided by ISO 17034 (ISO, 2016), the general requirements for the competence of reference material producers, and Guide 35 (ISO, 2017) providing guidance to characterisation studies, the assessment of homogeneity and stability, along with the treatment of data. ISO 17034 accredited products provide the user with additional confidence and assurance that the manufacturer has complied with an internationally established best practice approach. The demonstration of the competence of the reference material producer is a basic requirement for ensuring the quality of the reference materials are fit for purpose for the application.

Within the ISO17034 framework, the reference material producer is fully responsible for the planning, management and assignment of property values of the CRM. In the minerals sector, results from multiple commercial and mine site laboratory round-robins are often used for the determination of certified values and their associated uncertainties, following a rigorous statistical process. Confidence in the results and metrological traceability are also established through the use of ISO 17025 (ISO, 2017) accredited laboratories. The certified, consensus or target value for each analyte of interest is established from the mean or median of laboratory means. Each certified value must also include an assessment of its uncertainty or variance. Table 1 shows a typical CRM where a number of statistical parameters are shown.

TABLE 1 – Extract from Reference Material Certificate PBS-222, manufactured by IMS.

Analyte	Certified Value (y)	Standard Deviation		95% Confidence Interval (CI)		U_{CRM}	k	U_{CRM}	No. of Labs (ISO 17025)	No. Samples
		1 SD (s)	1 SD Within Lab (s_w)	lower	upper					
Fe	52.08	0.168	0.113	51.97	52.18	0.14	2	0.28	10	30
SiO ₂	9.33	0.049	0.023	9.30	9.36	0.040	2	0.081	10	29
Al ₂ O ₃	9.60	0.082	0.034	9.54	9.65	0.038	2	0.077	10	30
TiO ₂	0.760	0.0098	0.0020	0.752	0.768	0.0056	2	0.011	10	30
Mn	0.126	0.0065	0.0022	0.121	0.131	0.0024	2.26	0.0054	9	27
CaO	0.073	0.0045	0.0027	0.070	0.076	0.010	2.26	0.023	9	27
P	0.039	0.0009	0.0004	0.038	0.040	0.0011	2	0.0023	10	30
S	0.034	0.0025	0.0004	0.031	0.037	0.0018	2.31	0.0042	8	24

Accompanying each analyte certified value (y), a number of statistical parameters related to uncertainty are also listed. Uncertainty is fundamentally a measurement of the doubt in the certified value, and each of these parameters represent uncertainty in different ways.

- Standard deviation (s) is the measure of spread of analyte determinations and includes inter-laboratory bias, method uncertainty, and material homogeneity uncertainty. Approximately 95% of determinations using the same analytical method are expected to be between two standard deviations either side of the certified value. The standard deviation is calculated from the validated laboratory group data less outlier laboratory and individual determinations.
- Within laboratory standard deviation (s_w) is the average spread of determination values across the reporting laboratories, less outlier laboratory and individual determinations. This is calculated by single factor ANOVA of the participating laboratory groups.
- Confidence Interval (CI) is an estimate of the true (unknowable) analyte concentration in the material at the 95% confidence interval. For example, a 95% CI could be interpreted as there is a 0.95 probability that the true value is between certified value \pm CI. The narrower the interval, the more precise the certified value. The 95% CI should not be used for determination of quality control gates.

- Standard Uncertainty (U_{CRM}) is the sum of variance from characterisation, homogeneity and stability studies as shown in the formula below. The coverage Factor (k) is the students t-distribution value for two tailed test at 95%. The expanded Uncertainty (U_{CRM}) is the product of coverage factor and standard uncertainty, and represents the 95% confidence interval of the true unknowable analyte concentration of the batch combined with the bias from individual samples.

$$U_{CRM} = k \sqrt{u_{char}^2 + u_{hom}^2 + u_{stab}^2}$$

where;

- Uncertainty of characterisation (u_{char}) is the standard error of the mean of each laboratory's average analyte value. This is an estimate of the uncertainty of the CRM's true analyte value. A robust characterisation study that includes laboratories that are ISO 17025 (2017) accredited satisfy the metrological traceability requirements of characterisation. The uncertainty of characterisation relates primarily to the uncertainties of the laboratory methods.
- Uncertainty of homogeneity (u_{hom}) is an estimate of the material variance, which incorporates analytical, within-unit, and between-unit uncertainty. This parameter is a property largely controlled by the quality of the certified reference material.
- Uncertainty of stability (u_{stab}) which includes uncertainties from both short-term and long-term storage, transport, and degradation variances. This is typically insignificant in an iron ore CRM as the material as packaged is inherently stable with respect to the other uncertainties.

HOMOGENEITY STUDY DESIGN

It follows, therefore, during the manufacture and certification of CRMs, u_{hom} is an important contributor to the total uncertainty budget. This parameter is directly related to the inherent quality of the reference material. Materials of natural origin like iron ores, are typically heterogeneous by nature. This heterogeneity may be evident chemically, mineralogically and across particle size divisions as shown in Figure 2. During manufacture, the aim of the reference material producer is to minimise the magnitude of the between-unit differences so that they are insignificant compared to uncertainties that arise from characterisation. In the case of crushed CRMs additional challenges arise because of the inherent particle and mineralogical properties of the natural materials when handled. For a crushed CRM to be useful as a laboratory quality control tool, the homogeneity needs to be carefully assessed and include both sample preparation and analytical steps.

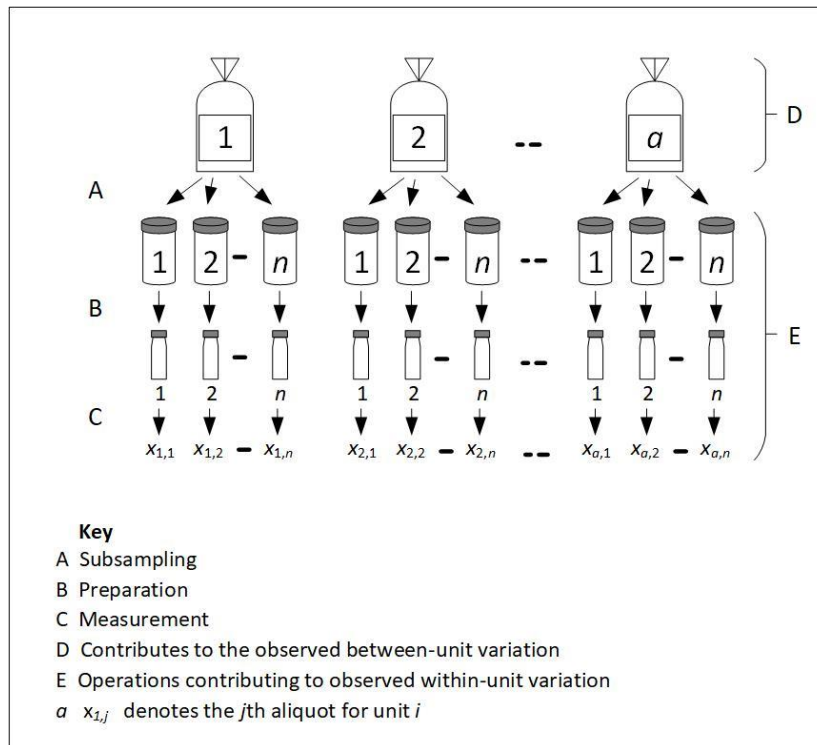


FIG 3. Schematic of a Homogeneity Study

Using a homogeneity study layout, such as in Figure 3, estimation of both *within sample variance* (S_w) and *between sample variance* (S_b) of multiple CRM units using analysis of variance (ANOVA) statistical techniques is possible. The apportioning of variance within and between a CRM unit is facilitated by the duplicate analysis of many samples. The total uncertainty of homogeneity (U_{hom}) is estimated as the square root of the sum of squared S_w and S_b variances (ISO Guide 35, 2017).

$$U_{hom} = \sqrt{S_b^2 + S_w^2}$$

Now that we have a measurement of the contributions to reference material homogeneity it is possible to use this figure to assess its quality and suitability for use in the laboratory as a QC tool. Uncertainty of homogeneity of a reference material can be assessed via either a statistical inference such as an F-test at the 95% level of confidence, or via reference to external criteria such as characterisation uncertainty or analytical measurement uncertainty by which the CRM will be used as a quality control tool. In the case of iron ore samples routinely measure using a lithium borate fusion and XRF analysis, ISO9516-1 (2003) can be referenced and compared.

ISO 9516-1 (2003) is a comprehensive procedure for the determination of the common elements required in the iron ore industry, and is applicable regardless of mineralogical type. The procedure documents sources of error in the method and tabulates permissible tolerances related to the uncertainty contributions of various components of the test method, including, but not exclusively, weighing, sample matrix and instrument conditions. The precision of the method is expressed by a series of regression equations unique to each element. The independent duplicate limit (R_d) is particularly relevant as the minimum uncertainty level of the method. This value can be used to compare to the homogeneity uncertainties determined by candidate reference materials as a measure of suitability, or fit for purpose, of the CRM as a laboratory quality control tool.

CRUSHED VS PULVERISED CRM PERFORMANCE

The uncertainty of homogeneity (U_{hom}) for a number of CRMs are shown in Figure 4. Pulverised ($n=10$) and crushed ($n=28$) iron-ore CRMs are plotted against the analyte concentration, and compared to the ISO9516-1 independent duplicate tolerance (R_d) for a few of the common elements significant to iron ore analysis.

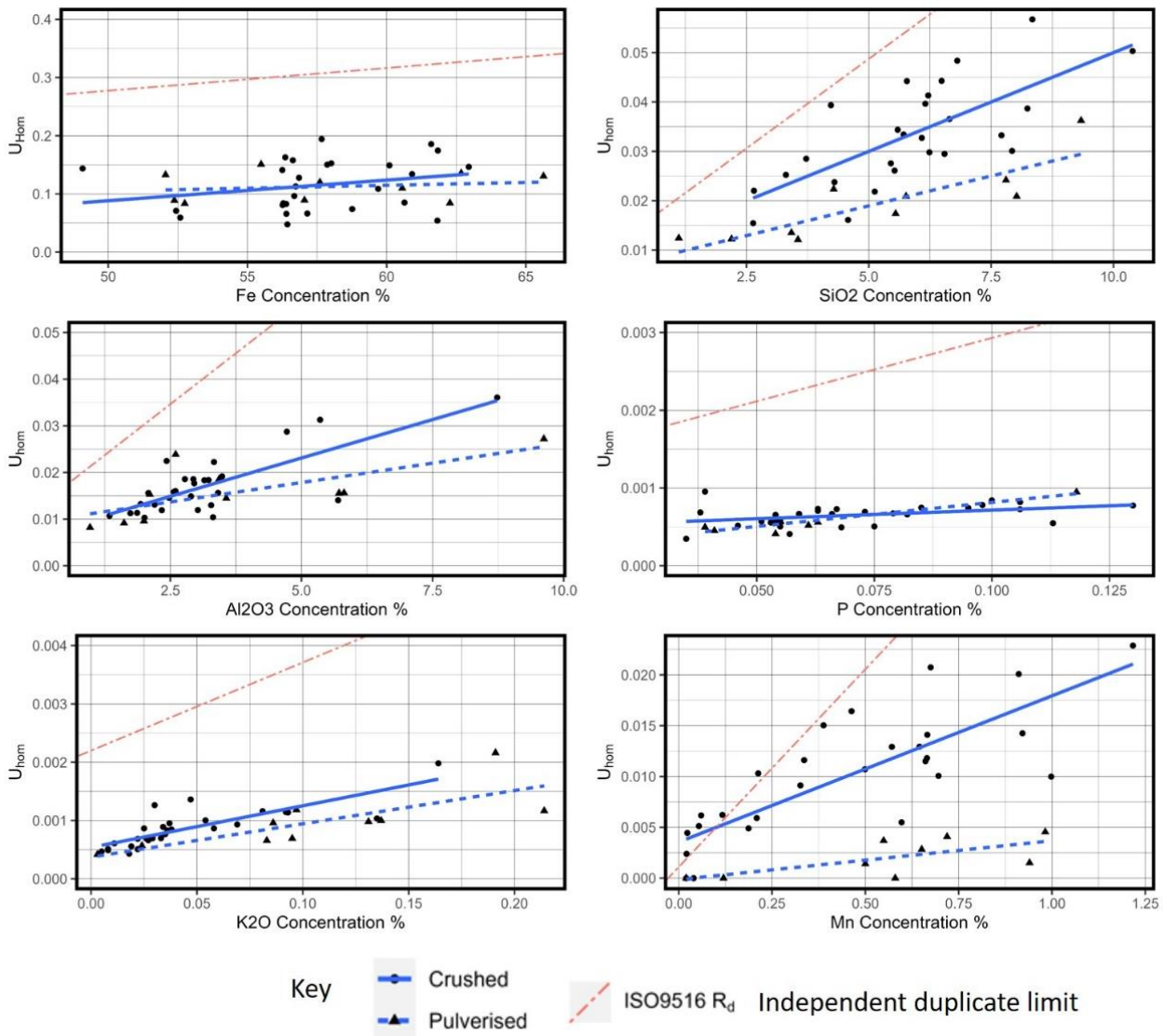


FIG 4 – Comparison of uncertainty of homogeneity (U_{hom}) of pulverised CRMs and crushed CRMs to the independent duplicate limit of the method for some key iron ore elements.

The data presented in Figure 4 has been collated from commercially produced batches for which a detailed homogeneity study was completed. Randomly selected samples from the production of each reference material were submitted to a single laboratory and multiple analyses completed utilising a regime schematically shown in Figure 3. Where a crushed CRM was submitted, the process included sample preparation steps (crushing, splitting and pulverisation) with duplicate analysis occurring at the analytical stage. All participating laboratories in these homogeneity studies have ISO17025 (2017) accreditation for iron ore by lithium borate fusion – XRF. Linear regression lines are displayed for both pulverised (dashed) and crushed (solid) CRM.

Figure 4 demonstrates that the comparison of pulverised to crushed CRM homogeneity are not consistent across each element. In the case of iron (Fe), the performance of a crushed reference material is very similar to a pulverised reference material, and trends similarly to the method tolerance, in a slight upward trend as iron concentration increases. In both pulverised and crushed CRM types, the material homogeneity is significantly less than the ISO 9516-1 (2003) method tolerance.

Overall, pulverised and crushed CRMs have no significant difference in total homogeneity for almost all analytes. This is an important point as it demonstrates a crushed CRM is a valuable quality control tool for determining whole of laboratory performance and can provide confidence and assurance of quality during both sample preparation and analytical processes.

In all cases, for crushed and pulverised CRMs, the homogeneity uncertainty was under the ISO9516-1 independent duplicate limit for XRF analysis, with the exception of Mn at the low level for crushed CRMs.

The notable exceptions to the U_{hom} parity between pulverised and crushed CRM are SiO_2 and Mn. An investigation into the source of the discrepancy for SiO_2 and Mn is not within the scope of this paper, however, by comparing the trends across multiple analytes we can surmise there may be a combination of mineralogical or textural characteristics that have an impact on adverse sample preparation outcomes.

CASE STUDY: SAMPLE PREPARATION BIAS

To demonstrate the effectiveness of crushed reference materials as a quality control tool, a case study was published for sample preparation and analysis in an iron ore laboratory (Independent Mineral Standards, 2021). In the laboratory performing the analysis, an automated crushing and pulverisation system was employed to prepare the samples, followed by fused bead-XRF analysis. The results for a crushed CRM were plotted over time on a quality control, or Shewhart chart, as shown in Figure 5. An excursion outside the control limits for key elements Fe, SiO_2 and Al_2O_3 was observed over a particular time period.

The control charts identify four samples failing with high Fe (>3 x standard deviation from the expected value). The same samples also fail low for both SiO_2 and Al_2O_3 . The fines of this CRM are known to contain elevated concentrations of SiO_2 and Al_2O_3 compared to that of the entire sample. Interrogation of the sample preparation system log files showed that all four samples failing QC passed through the same crusher. The laboratory had three crushers installed. Investigation of this crusher showed that a vacuum valve, open during cleaning, was damaged and was not closing fully while processing the sample. This was causing loss of the fines in the sample, leading to depression of SiO_2 and Al_2O_3 and elevation of Fe.

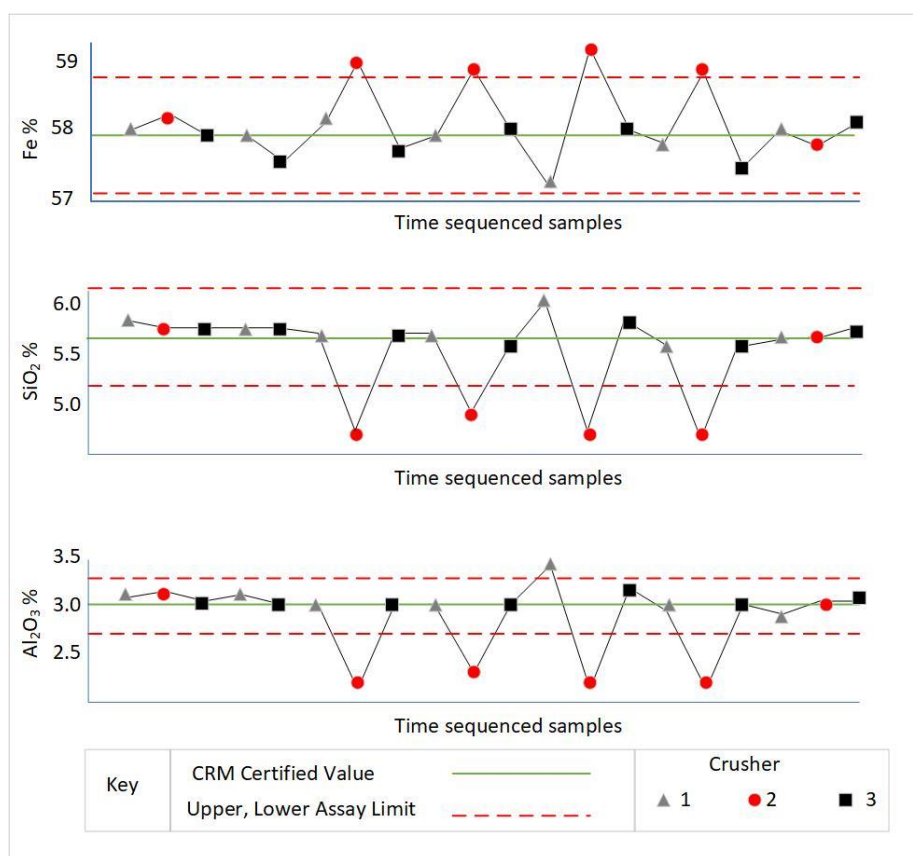


FIG 5 - Shewhart chart for Fe, SiO_2 and Al_2O_3 for 20 samples demonstrating a sample bias due to a crusher fault.

The case study demonstrates that a systematic sample preparation bias was occurring due to the preferential loss of material during crushing. The crushed CRM, when used in conjunction with a pulverised CRM for analysis, will therefore provide visibility of both precision and bias throughout the entire laboratory, and can help identify sample preparation issues that have a bearing on the quality of the analytical results. It would be very difficult to detect this issue in routine samples. If there were sample duplicates or splits taken, they would be collected after the crushing step, and as a result, both samples would be biased in this case.

The detection of loss in SiO₂ in the crusher is more interesting considering the U_{hom} data in Figure 4. In this case the between sample homogeneity, and analytical method precision are both sufficiently low for the detection of a bias caused by the crusher. The result demonstrates the quality of the CRM used has a level of homogeneity sufficiently fit for purpose to detect an adverse condition during the preparation of routine samples.

CONCLUSIONS

The use of certified reference materials (CRM) is critical to establishing a robust quality control program for iron ore projects. It is important for reference material manufacturers to assess the homogeneity characteristics of the CRM and demonstrate fit for purpose quality. A comparison of the homogeneity of crushed CRMs to pulverised CRMs demonstrates they are a suitable choice for whole of laboratory quality assessment, and are capable of detecting failures within sample preparation that may contribute to data quality.

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