

Reference Material Certificate: Pulverised Iron Ore PBS-222

Table 1: PBS-222 Certified Values expressed as % w/w

Analyte	Certified Value (y)	Standard Deviation (s)		95% Confidence Interval (CI)		U_{CRM}^{\wedge}	k#	U_{CRM}^{\sim}	No. of Labs (ISO 17025)	No. Samples
		1 SD	1 SD Within Lab	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
MgO	0.080	0.0085	0.0045	0.074	0.086	0.011	2	0.023	10	30
K ₂ O	0.024	0.0032	0.0005	0.021	0.026	0.010	2	0.020	10	30
Na ₂ O	0.027	0.0078	0.0043	0.020	0.035	0.011	2.45	0.027	6	18
As	0.005	0.0013	0.0006	0.004	0.007	0.0012	2.57	0.0032	5	15
Sr	0.008	0.0014	0.0009	0.006	0.010	0.0015	2.57	0.0039	5	15
V	0.007	0.0011	0.0004	0.006	0.009	0.0012	2.57	0.0032	5	15
Zn	0.002	0.0008	0.0005	0.001	0.003	0.0011	2.45	0.0026	6	17
LOI ₃₇₁	2.68	0.042	0.011	2.60	2.69	0.049	2.36	0.12	7	21
LOI ₆₅₀	4.84	0.040	0.020	4.81	4.88	0.032	2.36	0.077	7	21
LOI ₁₀₀₀	5.22	0.142	0.063	5.13	5.32	0.053	2	0.11	10	30
LOI _{425 to 650}	1.86	0.276	0.045	1.40	2.13	0.077	2.57	0.20	5	15
LOI _{650 to 1000}	0.30	0.040	0.015	0.27	0.34	0.020	2.36	0.047	7	21

Note 1. SI units equivalent: 1 ppm, parts per million \equiv grams per ton \equiv mg/kg \equiv ug/g \equiv 0.0001 % w/w \equiv 1000ppb, parts per billion
 Note 2. The number of decimal places quoted does not imply accuracy of the certified value to this level but are given to minimise rounding errors when calculating 2SD and 3SD.

\wedge Standard uncertainty.

Coverage Factor.

\sim Expanded Uncertainty.

Table 2: PBS-222 Informational Values expressed as % w/w

Analyte	Certified Value (y)	Standard Deviation (s)		95% Confidence Interval (CI)		U_{CRM}^{\wedge}	k#	U_{CRM}^{\sim}	No. of Labs	No. Samples
		1 SD	1 SD Within Lab	lower	upper					
Ba	0.002	0.0013	0.0010	0	0.005	0.0016	3.18	0.0051	3	8
Cl	0.007	0.0013	0.0012	0.005	0.008	0.0021	2.45	0.0052	6	16
Co	0.001	0.0004	0.0005	0.001	0.001	0.0011	2.78	0.0030	4	10
Cr	0.007	0.0012	0.0009	0.006	0.008	0.0015	2.45	0.0037	6	18
Cu	0.002	0.0012		0	0.016	0.0015	4.3	0.0064	2	6
Ni	0.002	0.0004	0.0004	0.002	0.002	0.0014	2.57	0.0036	5	15
Pb	0.003	0.0017	0.0011	0	0.007	0.0014	3.18	0.0044	3	9
Sn	0.002	0.0017		0	0.022	0.0018	4.3	0.0078	2	4
Zr	0.018	0.0032	0.0022	0.015	0.020	0.0015	2.31	0.0035	8	24
LOI425	2.94	0.039	0.012	2.89	3.02	0.040	2.78	0.11	4	12
LOI371 to 425	0.32	0.075	0.006	0.19	0.45	0.049	2.78	0.14	4	12

Version History

Batch	Author	Document Version	Date	Modifications
PBS222	H. Ooi	PBS222_Certificate_R0	17/08/2022	Initial Document
PBS222	H. Ooi	PBS222_Certificate_R1	20/03/2023	U_{CRM} rounded to two significant figures

Introduction

This document specifies preparation, analysis, and certification of pulverised reference material.

Material and Method of Preparation

PBS-222 is manufactured from a pulverised blend of iron ore materials from the Pilbara region of Western Australia. The material underwent a multi-stage crushing, pulverisation and screening prior to homogenisation process and discharge into storage containers. During the discharge the material was sub-sampled at regular intervals from which homogeneity and characterisation samples were drawn.

The samples taken were randomised before being submitted to independent ISO/IEC 17025 accredited laboratories for homogeneity and inter-laboratory round-robin testing.

Homogeneity Analysis

A homogeneity study was undertaken in accordance with ISO Guide 35:2017 and ISO17034:2016 using systematically selected samples to be representative of the entire batch. The sample identifiers were randomised to ensure different production order and laboratory analytical order. These samples were submitted to a single laboratory for multiple analysis in a single batch under repeatable conditions. The homogeneity study results were reviewed to ensure all analytes were deemed homogeneous prior to the material progressing to the inter-laboratory round-robin stage for characterisation assessment. A summary of the study is presented in Table 3 with results summarised in Table 4.

Table 3: Homogeneity Study Parameters

Attribute	Value
Sample mass /unit	10g
No. samples submitted	25
No. determinations per sample	2

Table 4: Homogeneity Study Results

Analyte	Mean Concentration Homogeneity Lab (% w/w)	SD between samples median value	Relative SD %
Fe	52.06	0.075	0.1
SiO ₂	9.34	0.032	0.3
Al ₂ O ₃	9.62	0.022	0.2
TiO ₂	0.746	0.0040	0.5
Mn	0.120	0.0000	0.0
CaO	0.070	0.0014	2.0
P	0.039	0.0004	0.9
S	0.039	0.0005	1.3
MgO	0.088	0.0024	2.8
K ₂ O	0.024	0.0005	2.0
Zn	0.002	0.0002	8.1
Cu	0.001	0.0000	0.0
Ba	0.003	0.0009	27
V	0.007	0.0004	5.1
Cr	0.007	0.0004	6.1
Cl	0.008	0.0016	20
As	0.003	0.0004	11
Ni	0.003	0.0006	23
Co	0.001	0.0003	24
Sr	0.011	0.0007	6.5
Zr	0.018	0.0004	2.1
Na ₂ O	0.016	0.0038	23.8
LOI ₃₇₁	2.91	0.020	0.7
LOI _{371 to 425}	1.32	0.022	1.7
LOI ₄₂₅	4.23	0.034	0.8
LOI _{425 to 650}	0.68	0.035	5.2
LOI ₆₅₀	4.90	0.023	0.5
LOI _{650 to 1000}	0.27	0.007	2.6
LOI ₁₀₀₀	5.17	0.025	0.5

Material Characterisation and Certification Methodology

A total of 30 x 10g samples were selected for inter-laboratory round-robin analysis, 3 samples were provided to 10 ISO17025 accredited laboratories. Laboratories analysed samples via Fusion XRF & TGA. 10 laboratories returned results in this round.

The process of characterisation was undertaken in accordance with ISO Guide 35:2017 and ISO17034:2016 following examination of grouped laboratory results for potential technical failures by way of comparison with the established CRM submitted for analysis with the candidate material. Where required, further investigation of outliers was conducted. Laboratory results deemed technical outliers were removed from the analysis pool prior to the determination of statistical parameters. The certifying officer, in some cases, may use their judgment in identifying or eliminating outliers outside of these statistical parameters.

- Certified value was determined by average of lab averages for analytes with no outlier laboratory results, or median of median for those with outlier laboratory results.
- 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.
- 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. The uncertainty of characterisation is derived from the standard deviation of average of laboratory averages divided by the square root of the number of laboratories. Uncertainty of material homogeneity (U_{hom}) is the sum of ANOVA within and between sample uncertainty derived from the homogeneity study. An allowance for stability has been included in accordance with ISO Guide 35.
- Coverage Factor (k) is the students t-distribution value for two tailed test at 95%.
- 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.

The certified value of any elemental or oxide concentration may not be negative even though in some cases the uncertainty error bounds define a range less than 0%. These cases are due to low concentrations of some analytes relative to the analytical detection limits and increments of precision.

Analytes have been categorised as Certified or Informational based on:

- Confirmation of sufficient between-unit variance demonstrating material homogeneity.
- Minimum number of participating ISO17025 accredited laboratories for that particular analyte.
- Sufficient agreement between participating laboratories.

Participating Laboratories

Laboratories used in the certification process are listed in Table 5 in alphabetical order, along with batch number.

Table 5: PBS-222 Participating Laboratories

Laboratory Name	Location	Job #
ALS Brisbane	Queensland, Australia	BR22086237
ALS Loughrea	Co Galway, Ireland	LR22098761
ALS Malaga	Western Australia	PH22081343
BV Canning Vale	Western Australia	u333981
BV Whyalla	South Australia	wh078654
BV Wingfield	South Australia	aa054717
Intertek Genalysis Maddington	Western Australia	1771_0_2206830
PT Intertek Utama Services	Jakarta, Indonesia	221295
SGS Newburn	Western Australia	WM211356
Spectrolab	Western Australia	PBS222

Intended Use

This iron ore reference material is intended for routine quality control (QC) monitoring of the accuracy and precision of XRF/TGA analysis. Crushed iron ore reference materials are used to determine the laboratory's ability to prepare, sub-sample and analyse. The combination of crushed and pulverised iron ore reference materials when inserted into runs of test samples is recommended as part of QC monitoring.

The estimate of material and measurement uncertainties reported in this certificate are the product of the participating laboratories, not any individual laboratory. Commercial laboratories typically have different measurement uncertainties to site-based laboratories. Application of the grouped uncertainties reported in this certificate to a specific laboratory for ongoing QC may lead to many false reports of out-of-control processes, or alternatively non reporting of out-of-control processes.

It is recommended that the centre line and control limits of a Shewhart chart used for ongoing monitoring of a particular laboratory are derived from averaged values and variation from replicate analysis of this CRM after removal of outliers.

Preparer and supplier of reference material

This reference material has been prepared and is certified by:

Independent Mineral Standards Pty Ltd
 16-18 Durham Rd
 Bayswater, WA 6053
 Australia

www.imstandards.com.au

The material has been supplied in 1kg press sealed plastic jars with labels showing batch number. Packaging into heat sealed mylar bags is available.

Minimum Sample Mass

This reference material has been certified using 0.2g to 0.5g aliquots for Li-B fusion XRF analysis. Uncertainty and homogeneity statements relating to this are only applicable if a minimum of 0.2g sample mass is used during Li-B fusion XRF analysis.

Period of Validity

This Certificate is valid 5 years from the date of original issue.

Commutability

This pulverised reference material is not commutable to any other analytical methods than as stated by its intended use.

Metrological Traceability

Metrological traceability of the assigned property values and their uncertainties has been established through an unbroken chain to the SI unit kilogram for Certified Values in Table 1. This is achieved through the use of assay laboratories accredited for ISO17025 for both the analytical method and analyte used in homogeneity, characterisation and stability studies.

Metrological traceability of the informational values and their uncertainties listed in Table 2 has not been established as values from laboratories and methods not accredited to ISO 17025 have been included in the characterisation studies. The values were incorporated to ensure sufficient number of participating laboratories to determine an uncertainty.

Stability and Storage Instructions

This CRM is an oxidised reference material and is stable in the sealed aluminised plastic bags, or press-sealed plastic jars under normal conditions of storage. It is recommended to keep jars sealed at all times when not in use.

Instructions for Correct Use

The recommended values for this CRM refer to the concentration levels after removal of hygroscopic moisture by drying in air to constant mass at 105°C. If the reference material is not dried prior to analysis, the recommended value should be corrected to the moisture bearing basis.

Legal notice

Independent Mineral Standards Pty Ltd has prepared and statistically evaluated the property values of this reference material to the best of ability. The purchaser by receipt hereof releases and indemnifies Independent Mineral Standards Pty Ltd from and against all liability and costs from the use of this material and information.

Certifying officer

Bruce Armstrong

Certification date

17th August 2022.

References

ISO Guide 35:2017, Reference materials – General and statistical principles for certification.

ISO17034:2016, General Requirements for the competence of reference material producers.