ORE RESEARCH & EXPLORATION P/L · ABN 28 006 859 856
37A Hosie St · Bayswater North · VIC · 3153 · AUSTRALIA
☎ 61 3 9729 0333 ℻ 61 3 9729 8338
ⓘ info@ore.com.au 🌐 www.ore.com.au

CERTIFICATE OF ANALYSIS FOR

Zinc Concentrate (McArthur River Mining operation, NT, Australia)
CERTIFIED REFERENCE MATERIAL
OREAS 351

Table 1. Certified Values, SDs, 95% Confidence and Tolerance Limits for OREAS 351.

Constituent	Certified Value	1SD	95% Confidence Limits		95% Tolerance Limits	
			Low	High	Low	High
Umpire Labs (dry sample basis)						
*Acid Digestion Titration**						
Zn, Zinc (wt.%)	46.97	0.155	46.88	47.06	46.93	47.01
Commercial Labs (‘as received’ sample basis)						
4-Acid Digestion						
Ag, Silver (ppm)	120	3	118	121	117	122
As, Arsenic (ppm)	1076	44	1049	1102	1050	1102
Bi, Bismuth (ppm)	< 5	IND	IND	IND	IND	IND
Cd, Cadmium (ppm)	1095	51	1059	1131	1075	1115
Cu, Copper (wt.%)	1.07	0.024	1.06	1.08	1.05	1.09
Fe, Iron (wt.%)	5.88	0.209	5.76	6.00	5.76	6.00
Mg, Magnesium (wt.%)	0.078	0.008	0.073	0.082	0.076	0.079
Pb, Lead (wt.%)	3.85	0.070	3.81	3.89	3.78	3.92
Sb, Antimony (ppm)	144	20	130	158	139	149
Tl, Thallium (ppm)	144	13	136	152	139	149
Zn, Zinc (wt.%)	46.99	1.262	45.51	48.47	46.05	47.93
Peroxide Fusion ICP						
SiO_2, Silicon dioxide (wt.%)	5.07	0.264	4.91	5.23	4.95	5.18
Infrared Combustion						
S, Sulphur (wt.%)	31.84	0.648	31.38	32.29	31.48	32.20

*Except for one laboratory that used borate fusion XRF.

SI unit equivalents: ppm, parts per million ≡ mg/kg ≡ µg/g ≡ 0.0001 wt.% ≡ 1000 ppb, parts per billion.

Note 1: intervals may appear asymmetric due to rounding.

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 windows.

Table 2. Indicative Values for OREAS 351.

Constituent	Unit	Value	Constituent	Unit	Value	Constituent	Unit	Value
Umpire Labs (dry sample basis)								
Acid Digestion Titration								
Pb	wt.%	*3.99*						
Thermogravimetry								
H_2O-	wt.%	*0.737*						
Other Mineral Labs (as received basis)								
4-Acid Digestion								
Al	wt.%	*0.492*	La	ppm	*3.00*	Se	ppm	*< 5*
Ba	ppm	*14.0*	Li	ppm	*< 5*	Sn	ppm	*< 10*
Be	ppm	*0.50*	Mn	wt.%	*0.004*	Sr	ppm	*3.00*
Ca	wt.%	*0.090*	Mo	ppm	*5.80*	Te	ppm	*< 5*
Ce	ppm	*< 10*	Na	wt.%	*0.020*	Ti	wt.%	*0.023*
Co	ppm	*28.4*	Nb	ppm	*< 10*	U	ppm	*< 10*
Cr	ppm	*15.0*	Ni	ppm	*11.0*	V	ppm	*11.0*
Ga	ppm	*12.4*	P	wt.%	*0.008*	W	ppm	*< 10*
Ge	ppm	*< 10*	Re	ppm	*< 5*	Y	ppm	*1.00*
In	ppm	*< 10*	S	wt.%	*31.83*	Zr	ppm	*13.0*
K	wt.%	*0.340*	Sc	ppm	*1.00*			
Peroxide Fusion ICP								
Al	wt.%	*0.460*	Fe	wt.%	*5.78*	S	wt.%	*33.15*
As	ppm	*1044*	K	wt.%	*0.360*	Sb	ppm	*68*
Ca	wt.%	*0.074*	Mg	wt.%	*0.091*	Sr	ppm	*< 50*
Cd	ppm	*1015*	Mn	wt.%	*< 0.01*	Ti	wt.%	*0.020*
Co	ppm	*30.0*	Ni	ppm	*< 50*	Zn	wt.%	*52.84*
Cu	wt.%	*1.07*	Pb	wt.%	*3.94*			

SI unit equivalents: ppm, parts per million ≡ mg/kg ≡ µg/g ≡ 0.0001 wt.% ≡ 1000 ppb, parts per billion.

Note: the number of significant figures reported is not a reflection of the level of certainty of stated values. They are instead an artefact of ORE's in-house CRM-specific LIMS.

INTRODUCTION

OREAS reference materials are intended to provide a low cost method of evaluating and improving the quality of analysis of geological samples. To the geologist they provide a means of implementing quality control in analytical data sets generated in exploration from the grass roots level through to prospect evaluation, and in grade control at mining operations. To the analyst they provide an effective means of calibrating analytical equipment, assessing new techniques and routinely monitoring in-house procedures.

OREAS reference materials enable users to successfully achieve process control of these tasks because the observed variance from repeated analysis has its origin almost exclusively in the analytical process rather than the reference material itself.

SOURCE MATERIALS

OREAS 351 is a zinc concentrate certified reference material (CRM) prepared and certified by Ore Research & Exploration Pty Ltd. The material constituting OREAS 351 was sourced from the McArthur River Mining operation located in the Gulf of Carpentaria region in the Northern Territory of Australia. The mine is situated about 900 km southeast of Darwin. The major sulphides are pyrite, sphalerite and galena, with lesser chalcopyrite, arsenopyrite and marcasite.

COMMINUTION AND HOMOGENISATION PROCEDURES

The source materials constituting OREAS 351 were prepared in the following manner:

- Drying of materials to constant mass at 85°C;
- Deagglomeration and homogenisation;
- Packaging into 10g units sealed under nitrogen in laminated foil pouches.

ANALYTICAL PROGRAM

Sixteen ‘umpire’ laboratories employing classical wet chemistry methods and fourteen other mineral laboratories employing instrumental methods participated in the round robin certification program to certify the 14 analytes reported in Table 1.

The umpire laboratories each received a 30g sample and employed the following methods:

- Zinc was determined in 3 trials by ethylenediamminetetraacetic acid (EDTA) with titration finish (15 laboratories) or borate fusion with XRF finish (1 laboratory);
- Moisture (H_2O-) at 105°C by thermogravimetry (16 laboratories).

The umpire laboratories were given strict pre-assay sample instructions relating to moisture correction. These instructions included:

- Equilibration of sample material to lab atmosphere for a minimum of 2 hours;
- Hygroscopic moisture analysis at 105°C determined on a separate subsample and weighed for analysis at the same time as the sample aliquots for Zn as per ISO 9599.

The umpire laboratories were also requested to report metal concentrations on both a dry and moisture-bearing basis and include all results for moisture determinations. A value for moisture (H_2O-) is provided in the Indicative Values table for informational purposes only (see Table 2). **The certified value for zinc is on a dry sample basis.**

The commercial laboratories each received five 20g samples and employed the following methods:

- 4-acid digestion (HF-HNO_3-$HClO_4$-HCl) with ICP-OES, ICP-MS or AAS finish for Ag, As, Bi, Cd, Cu, Fe, Mg, Pb, Sb, Tl and Zn (14 laboratories);
- Peroxide fusion with ICP-OES finish for SiO_2 (14 laboratories);
- Infrared combustion furnace for S (13 laboratories).

Samples for the round robin program were taken at five predetermined sampling intervals immediately following final homogenisation and are considered representative of the entire batch of OREAS 351. The five samples received by each laboratory were obtained by taking one 20g sample from each of the five sampling lots. Table 1 presents the 14 certified values together with their associated 1SD's, 95% confidence and tolerance limits and Table 2 shows 52 indicative values. Table 3 provides performance gate intervals for the certified values based on their pooled 1SD's. Tabulated results of all elements together with uncorrected means, medians, standard deviations, relative standard deviations and per cent deviation of lab means from the corrected mean of means (PDM[3]) are presented in the detailed certification data for this CRM (**OREAS 351 DataPack-1.1.180831_112159.xlsx**).

STATISTICAL ANALYSIS

Certified Values, Confidence Limits, Standard Deviations and Tolerance Limits (Table 1) have been determined for each analyte following removal of individual, laboratory dataset (batch) and 3SD outliers (single iteration). For individual outliers within a laboratory batch the z-score test is used in combination with a second method that determines the per cent deviation of the individual value from the batch median. Outliers in general are selected on the basis of z-scores > 2.5 and with per cent deviations (i) > 3 and (ii) more than three times the average absolute per cent deviation for the batch. In certain instances statistician's prerogative has been employed in discriminating outliers. Each laboratory data set mean is tested for outlying status based on z-score discrimination and rejected if >2.5. After individual and laboratory data set (batch) outliers have been eliminated a non-iterative 3 standard deviation filter is applied, with those values lying outside this window also relegated to outlying status.

Certified Values are the means of accepted laboratory means after outlier filtering. Indicative (uncertified) values (Table 2) are provided where i) the number of laboratories reporting a particular analyte is insufficient (< 5) to support certification; ii) inter-laboratory consensus is poor; or iii) a significant proportion of results are outlying.

95% Confidence Limits are inversely proportional to the number of participating laboratories and inter-laboratory agreement. It is a measure of the reliability of the certified value. A 95% confidence interval indicates a 95% probability that the true value of the analyte under consideration lies between the upper and lower limits. *95% Confidence Limits should not be used as control limits for laboratory performance.*

Standard Deviation values (1SDs) are reported in Table 1 and provide an indication of a level of performance that might reasonably be expected from a laboratory being monitored by this CRM in a QA/QC program. The SD values include all sources of measurement uncertainty: between-lab variance, within-run variance (precision errors) and CRM variability. For an effective CRM the contribution of the latter should be negligible in comparison to measurement errors. OREAS reference materials have a level of homogeneity such that the observed variance from repeated analysis has its origin almost exclusively in the analytical process rather than the reference material itself.

The SD for each analyte's certified value is calculated from the same filtered data set used to determine the certified value, i.e. after removal of any individual, lab dataset (batch) and 3SD outliers (single iteration). These outliers can only be removed after the absolute homogeneity of the CRM has been independently established, i.e. the outliers must be confidently deemed to be analytical rather than arising from inhomogeneity of the CRM. **The standard deviation is then calculated for each analyte from the pooled accepted analyses generated from the certification program.**

In the application of SD's in monitoring performance it is important to note that not all laboratories function at the same level of proficiency and that different methods in use at a particular laboratory have differing levels of precision. Each laboratory has its own inherent SD (for a specific concentration level and analyte-method pair) based on the analytical process and this SD is not directly related to the round robin program.

The majority of data generated in the round robin program was produced by a selection of world class laboratories. The SD's thus generated are more constrained than those that would be produced across a randomly selected group of laboratories. To produce more generally achievable SD's the 'pooled' SD's provided in this report include inter-lab bias. This 'one size fits all' approach may require revision at the discretion of the QC manager concerned following careful scrutiny of QC control charts.

Table 3 shows **Performance Gates** calculated for two and three standard deviations. As a guide these intervals may be regarded as warning or rejection for multiple 2SD outliers, or rejection for individual 3SD outliers in QC monitoring, although their precise application should be at the discretion of the QC manager concerned. A second method utilises a 5% window calculated directly from the certified value. Standard deviation is also shown in relative per cent for one, two and three relative standard deviations (1RSD, 2RSD and 3RSD) to facilitate an appreciation of the magnitude of these numbers and a comparison with the 5% window. Caution should be exercised when concentration levels approach lower limits of detection of the analytical methods employed as performance gates calculated from standard deviations tend to be excessively wide whereas those determined by the 5% method are too narrow. One approach used at commercial laboratories is to set the acceptance criteria at twice the detection level (DL) ± 10%.

i.e. Certified Value ± 10% ± 2DL (adapted from Govett, 1983)

Tolerance Limits (ISO Guide 3207) were determined using an analysis of precision errors method and are considered a conservative estimate of true homogeneity. The meaning of tolerance limits may be illustrated for Zn by the umpire laboratories employing EDTA digestion with titration, where 99% of the time ($1\text{-}\alpha=0.99$) at least 95% of subsamples ($\rho=0.95$) will have concentrations lying between 46.93 and 47.01 wt.%. Put more precisely, this means that if the same number of subsamples were taken and analysed in the same manner repeatedly, 99% of the tolerance intervals so constructed would cover at least 95% of the total population, and 1% of the tolerance intervals would cover less than 95% of the total population (ISO Guide 35). Based on the statistical analysis of the results of the inter-laboratory certification program it can be concluded that OREAS 351 is fit-for-purpose as a certified reference material (see 'Intended Use' below).

Table 3. Performance Gates for OREAS 351.

Constituent	Certified Value	Absolute Standard Deviations					Relative Standard Deviations			5% window	
		1SD	2SD Low	2SD High	3SD Low	3SD High	1RSD	2RSD	3RSD	Low	High
Umpire Labs (dry sample basis)											
*Acid Digestion Titration**											
Zn, wt.%	46.97	0.155	46.66	47.28	46.50	47.44	0.33%	0.66%	0.99%	44.62	49.32
Commercial Labs ('as received' sample basis)											
4-Acid Digestion											
Ag, ppm	120	3	114	125	111	128	2.40%	4.79%	7.19%	114	126
As, ppm	1076	44	987	1165	942	1209	4.14%	8.27%	12.41%	1022	1129
Bi, ppm	< 5	IND	IND	IND	IND	IND	IND	IND	IND	IND	IND
Cd, ppm	1095	51	992	1198	941	1249	4.69%	9.39%	14.08%	1040	1150
Cu, wt.%	1.07	0.024	1.02	1.12	1.00	1.14	2.26%	4.51%	6.77%	1.02	1.12
Fe, wt.%	5.88	0.209	5.46	6.30	5.25	6.51	3.55%	7.10%	10.66%	5.59	6.18
Mg, wt.%	0.078	0.008	0.062	0.094	0.054	0.102	10.27%	20.55%	30.82%	0.074	0.082
Pb, wt.%	3.85	0.070	3.71	3.99	3.64	4.06	1.81%	3.63%	5.44%	3.66	4.04
Sb, ppm	144	20	103	184	83	205	14.16%	28.33%	42.49%	136	151
Tl, ppm	144	13	118	170	104	184	9.17%	18.35%	27.52%	137	151
Zn, wt.%	46.99	1.262	44.47	49.52	43.20	50.78	2.69%	5.37%	8.06%	44.64	49.34
Peroxide Fusion ICP											
SiO_2, wt.%	5.07	0.264	4.54	5.60	4.27	5.86	5.22%	10.44%	15.66%	4.81	5.32
Infrared Combustion											
S, wt.%	31.84	0.648	30.54	33.13	29.89	33.78	2.04%	4.07%	6.11%	30.25	33.43

*Except for one laboratory that used borate fusion XRF.

SI unit equivalents: ppm, parts per million ≡ mg/kg ≡ µg/g ≡ 0.0001 wt.% ≡ 1000 ppb, parts per billion.

Note 1: intervals may appear asymmetric due to rounding.

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 windows.

PARTICIPATING LABORATORIES

1. *Actlabs, Ancaster, Ontario, Canada
2. ♦*AH Knight, St Helens, Merseyside, UK
3. ♦Alex Stewart International, Liverpool, UK
4. ♦ALS Inspection, Prescot, Merseyside, UK
5. ♦ALS, Burnie, TAS, Australia
6. ♦*ALS, Lima, Peru
7. *ALS, Perth, WA, Australia
8. *ALS, Vancouver, BC, Canada
9. ♦Bachelet, Angleur, Liege, Belgium
10. *Bureau Veritas Geoanalytical, Adelaide, SA, Australia
11. *Bureau Veritas Geoanalytical, Perth, WA, Australia

12. ♦Independent, Perth, WA, Australia
13. ♦*Inspectorate (BV), Lima, Peru
14. ♦Inspectorate (BV), Shanghai, Bao Shan District, China
15. ♦Inspectorate (BV), Witham, Essex, UK
16. *Intertek Genalysis, Perth, WA, Australia
17. ♦Intertek LSI, Rotterdam, Zuid-Holland, Netherlands
18. *Intertek Testing Services, Cupang, Muntinlupa, Philippines
19. *MinAnalytical Services, Perth, WA, Australia
20. ♦RC Inspection, Rotterdam, Netherlands
21. ♦*SGS Australia Mineral Services, Perth, WA, Australia
22. ♦*SGS Mineral Services, Townsville, QLD, Australia
23. ♦SGS Nederland B.V., Spijkenisse, Zuid-Holland, Netherlands
24. *Shiva Analyticals Ltd, Bangalore North, Karnataka, India
25. ♦SRL, Perth, WA, Australia

♦ *= Umpire laboratory (wet chemistry methods), * = Analytical laboratory (instrumental methods).*

PREPARER AND SUPPLIER OF THE REFERENCE MATERIAL

Reference material OREAS 351 has been prepared, certified and is supplied by:

ORE Research & Exploration Pty Ltd
37A Hosie Street
Bayswater North VIC 3153
AUSTRALIA

Tel: +613-9729 0333
Fax: +613-9729 8338
Web: www.ore.com.au
Email: info@ore.com.au

It is available in unit sizes of 10g sealed under nitrogen in laminated foil pouches.

INTENDED USE

OREAS 351 is intended for the following uses:

- For the monitoring of laboratory performance in the analysis of analytes reported in Table 1 in geological samples;
- For the verification of analytical methods for analytes reported in Table 1;
- For the calibration of instruments used in the determination of the concentration of analytes reported in Table 1.

STABILITY AND STORAGE INSTRUCTIONS

OREAS 351 is a sulphide-rich reference material (S ~31.8%) and is reactive under normal atmospheric conditions. To inhibit oxidation and prolong its shelf life it has been sealed under nitrogen in robust laminated foil pouches. In its unopened state under normal conditions of storage it has a shelf life beyond five years.

INSTRUCTIONS FOR CORRECT USE

The certified value for Zn by EDTA with titration is on a dry sample basis. There was considerable variation in moisture content reported by the laboratories (lab means varied from 0.24 to 1.53 wt.% H_2O-) and this can be a significant source of error if not properly controlled. Therefore, all analyses were performed on the samples after equilibration with the laboratory atmosphere for a minimum of 2 hours and hygroscopic moisture analysis at 105°C determined on a separate subsample and weighed for analysis at the same time as the sample aliquot for Zn as per ISO 9599. If the reference material is not dried prior to analysis, the EDTA with titration certified value for Zn should be corrected to the moisture-bearing basis.

As per routine analysis at commercial laboratories, the certified values derived by 4-acid digestion, peroxide fusion with ICP-OES (SiO_2 only) and infrared combustion furnace (S only) refer to the concentration levels in the packaged state. There is no need for drying prior to weighing and analysis.

HANDLING INSTRUCTIONS

Fine powders pose a risk to eyes and lungs and therefore standard precautions such as the use of safety glasses and dust masks are advised.

METROLOGICAL TRACEABILITY

The analytical samples were selected in a manner to represent the entire batch of prepared CRM. This 'representivity' was maintained in each submitted laboratory sample batch and ensures the user that the data is traceable from sample selection through to the analytical results that underlie the consensus values. Each analytical data set has been validated by its assayer through the inclusion of internal reference materials and QC checks during analysis.

The laboratories were chosen on the basis of their competence (from past performance in inter-laboratory programs undertaken by ORE Pty Ltd) for a particular analytical method, analyte or analyte suite, and sample matrix. Most of these laboratories have and maintain ISO 17025 accreditation. The certified values presented in this report are calculated from the means of accepted data following robust statistical treatment as detailed in this report.

Guide ISO/TR 16476:2016, section 5.3.1 describes metrological traceability in reference materials as it pertains to the transformation of the measurand. In this section it states, *"Although the determination of the property value itself can be made traceable to appropriate units through, for example, calibration of the measurement equipment used, steps like the transformation of the sample from one physical (chemical) state to another cannot. Such transformations may only be compared with a reference (when available), or among themselves. For some transformations, reference methods have been defined and may be used in certification projects to evaluate the uncertainty associated with such a transformation. In other cases,* ***only a comparison among different laboratories using the same method is possible. In this case, certification takes place on the basis of agreement among independent measurement results*** *(see ISO Guide 35:2006, Clause 10)."*

COMMUTABILITY

The measurements of the results that underlie the certified values contained in this report were undertaken by methods involving pre-treatment (digestion/fusion) of the sample. This served to reduce the sample to a simple and well understood form permitting calibration using simple solutions of the CRM. Due to these methods being well understood and highly effective, commutability is not an issue for this CRM. All OREAS CRMs are sourced from natural ore minerals meaning they will display similar behaviour as routine 'field' samples in the relevant measurement process. Care should be taken to ensure 'matrix matching' as close as practically achievable. The matrix and mineralisation style of the CRM is described in the 'Source Material' section and users should select appropriate CRMs matching these attributes to their field samples.

LEGAL NOTICE

Ore Research & Exploration Pty Ltd has prepared and statistically evaluated the property values of this reference material to the best of its ability. The Purchaser by receipt hereof releases and indemnifies Ore Research & Exploration Pty Ltd from and against all liability and costs arising from the use of this material and information.

DOCUMENT HISTORY

Revision No	Date	Changes applied
1	31st Aug, 2018	Combined DataPack release, reference to Govett added to Performance Gates section, Metrological Traceability and Commutability sections added.
0	5th Apr, 2016	First publication.

QMS ACCREDITED

ORE Pty Ltd is accredited to ISO 9001:2008 by Lloyd's Register Quality Assurance Ltd for its quality management system including development, manufacturing, certification and supply of CRMs.

CERTIFYING OFFICER

Craig Hamlyn (B.Sc. Hons - Geology), Technical Manager - ORE P/L

REFERENCES

Govett, G.J.S. (1983), ed. Handbook of Exploration Geochemistry, Volume 2: Statistics and Data Analysis in Geochemical Prospecting (Variations of accuracy and precision).

ISO Guide 30 (1992), Terms and definitions used in connection with reference materials.

ISO Guide 31 (2000), Reference materials – Contents of certificates and labels.

ISO Guide 3207 (1975), Statistical interpretation of data - Determination of a statistical tolerance interval.

ISO Guide 35 (2006), Certification of reference materials - General and statistical principals.