CERTIFICATE OF A REFERENCE MATERIAL

BASE METAL SULPHIDE ORE
OREAS 32

Constituent	Certified value	95% Confidence limits	
		High	Low
Copper, Cu (wt. %)	2.95	3.01	2.89
Lead, Pb (wt. %)	8.54	8.64	8.44
Zinc, Zn (wt. %)	12.68	12.77	12.59
Sliver, Ag (ppm)	566	580	552
Gold, Au (ppm)	2.61	2.71	2.51

Source and Description of Reference Material

Base metal sulphide ore reference material OREAS 32 is a composite of Pb-Zn-Ag ore and "blue quartz" rock from Minerals Mining and Metallurgy Ltd's South Mine at Broken Hill in western New South Wales and copper concentrate from Renison Goldfields Consolidated Ltd's Mount Lyell Mine at Queenstown, Tasmania. The Broken Hill South Mine is in strongly deformed, high grade metamorphics of the Lower Proterozoic Willyama Complex. The ore and blue quartz lode occur within a distinctive unit known as the lode horizon consisting of alternating ore lenses and sillimanite gneiss and quartzite layers. The major economic minerals are sphalerite and galena in association with pyrrhotite, chalcopyrite, arsenopyrite and loellingite. The Mount Lyell mineralisation is contained within a series of sheared and altered Cambrian acid lavas, intermediate to acid pyroclastics and cherts. They range from disseminated, low grade pyrite-chalcopyrite ores to richer bornite-chalcopyrite ores with massive and banded pyritic ores towards the top of the sequence.

Method of Preparation

The hand-picked Broken Hill ore and blue quartz rock were separately crushed to minus 6mm and dried at 105°C. The Mount Lyell copper concentrate was dried at 105°C and blended with the Broken Hill samples. The resultant mixture was finely ground, screened to 200 mesh (minus 75 microns), and blended.

The homogenised pulp was equilibrated with nitrogen in dessicators in line with a vacuum pump and N_2 gas supply, transferred to an inert gas enclosure and sealed under nitrogen in laminated foil pouches.

Statement of Homogeneity

Constituent:	Certified Value	Tolerance limits $1-\alpha = 0.99$, $p = 0.95$	
		High	Low
Copper, Cu (wt.%)	2.95	3.00	2.90
Lead, Pb (wt. %)	8.54	8.65	8.43
Zinc, Zn (wt. %)	12.68	12.85	12.51
Silver, Ag (ppm)	566	575	557
Gold, Au (ppm)	2.61	2.94	2.28

The standard deviation of each laboratory data set includes error due both to the imprecision of the analytical method employed and to possible inhomogeneity of the material analysed. The standard deviation of the pooled individual analyses of all participating laboratories includes error due to the imprecision of each analytical method, to possible inhomogeneity of the material analysed and, in particular, to inaccuracy of each analytical method. In the case of Cu, Pb, Zn and Ag, where analytical subsample portions (generally 0.2-1.0g) are small relative to unit size (50g), the within-unit inhomogeneity is an important consideration, whereas that between units is considered negligible in this instance. In determining the tolerance intervals for Cu, Pb, Zn and Ag the component of error attributable to measurement innaccuracy was eliminated by transformation of the individual results of each data set to a common mean (the uncorrected grand mean) according to the formula

$$x_{ij}' = x_{ij} - \bar{x}_i + \frac{\sum_{i=1}^{p} \sum_{j=1}^{n_i} x_{ij}}{\sum_{i=1}^{p} n_i}$$

where

x_{ij} *is the jth raw result reported by laboratory i;*

x_{ij}' *is the jth transformed result reported by laboratory i;*

n_i *is the number of results reported by laboratory i;*

p *is the number of participating laboratories;*

$\bar{x}_i$ *is the raw mean for laboratory i.*

Implicit in this treatment is the assumption that between-unit inhomogeneity is negligible relative to within-unit inhomogeneity and measurement errors.

Gold is a trace constituent in this material and, unlike Cu, Pb, Zn and Ag, analytical subsample portions are high (10-30g) relative to unit size. For this reason between-unit inhomogeneity is a potentially significant source of error. Accordingly, the gold data were not transformed to a common mean prior to the calculation of tolerance limits.

The homogeneity of each constituent was determined from tables of factors for two-sided tolerance limits for normal distributions (ISO 3207) in which

$$\text{Lower limit is } \bar{x} - k_2'(n,p,1-\alpha)s_g'$$
$$\text{Upper limit is } \bar{x} + k_2'(n,p,1-\alpha)s_g'$$

where

n is the number of results;

1-α is the confidence level;

p is the proportion of results expected within the tolerance limits;

k_2' *is the factor for two-sided tolerance limits (m,σ unknown);*

s_g' *is the corrected grand standard deviation.*

The meaning of these tolerance limits may be illustrated for copper, where 99% of the time at least 95% of subsamples will have concentrations lying between 2.90 and 3.00 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).

The corrected grand standard deviation, S_g'', used to compute the tolerance intervals is the weighted means of standard deviations of all data sets for a particular constituent according to the formula

$$s_g' = \frac{\displaystyle\sum_{i=1}^{p} \left(s_i\left(1-\frac{s_i}{s_g'}\right)\right)}{\displaystyle\sum_{i=1}^{p} \left(1-\frac{s_i}{s_g'}\right)}$$

where

$\left(1 - \dfrac{s_i}{s_g'}\right)$ *is the weighting factor for laboratory i;*

s_g' *is the grand standard deviation computed from the transformed (i.e. means-adjusted) results for Cu, Pb, Zn, Ag, and the raw results for Au,*

according to the formula

$$s_g' = \left[\frac{\displaystyle\sum_{i=j}^{p}\sum_{j=i}^{n_i} (x_{ij}' - \bar{x}_i')^2}{\displaystyle\sum_{i=1}^{p} n_i - 1}\right]^{\frac{1}{2}}$$

where $\bar{x}_i'$ is the transformed mean for laboratorty i

The weighting factors were applied to compensate for the considerable variation in analytical precision amongst the methods employed. This is illustrated below for zinc where the means and standard deviations of each data set (each based on 10 replicate determinations) are graphically compared. The

standard deviations of those laboratories employing titrimetric methods (codes A to H) are generally less than that of other methods indicating the superior analytical precision of the former. Accordingly, most of the variance observed in the results of laboratories I to X can be attributed to measurement error rather than inhomogeneity of the reference material. Therefore, in the calculation of tolerance intervals weighting factors for each data set have been constructed so as to be inversely proportional to the standard deviation of that data set.

No individual outliers were removed from the results prior to the calculation of tolerance intervals, however, a weighting factor of zero was applied to those data sets where $s_i/s_g'>1$ (i.e. where the weighting factor $(1-s_i/s_g')<0$).

In the case of gold, where no correction was applied to compensate for that component of error resulting from measurement innaccuracy, the tolerance intervals are considered to be a conservative estimate of homogeneity.
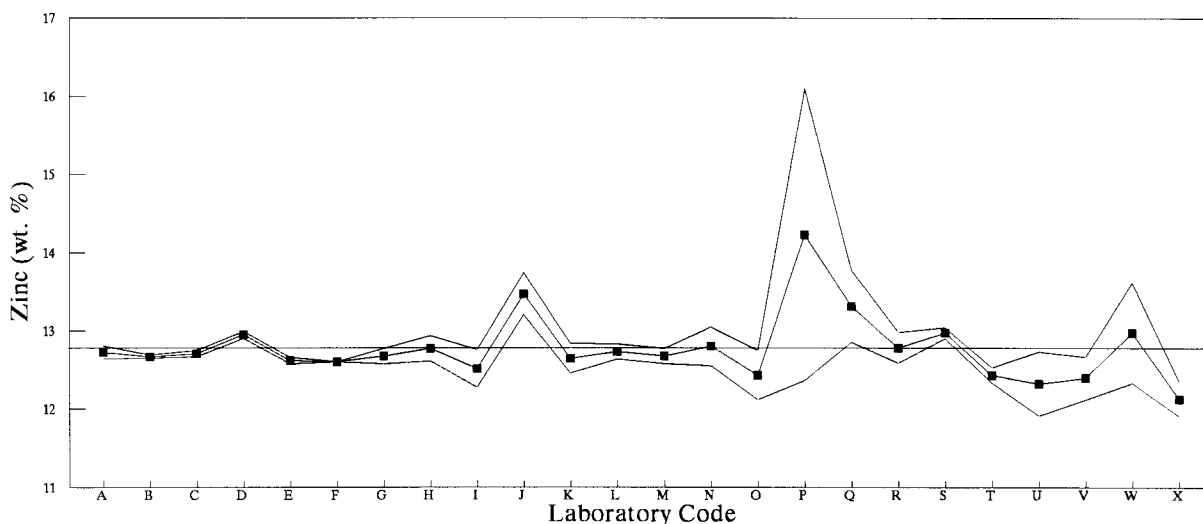
Mean zinc concentration in OREAS 32 plotted for each laboratory data set of ten replicates. The upper and lower curves represent the two sigma standard deviation either side of each mean. The horizontal line is the uncorrected grand mean.

Estimator and Confidence Limits of the Certified Value

The certified value is the mean of means of accepted replicate values of accepted participating laboratories computed according to the formulae

$$\bar{x}_i = \frac{1}{n_i} \sum_{j=1}^{n_i} x_{ij}$$

$$\bar{\bar{x}} = \frac{1}{p} \sum_{i=1}^{p} \bar{x}_i$$

where

x_{ij} *is the jth result reported by laboratory i;*

p is the number of participating laboratories;

n_i *is the number of results reported by laboratory i;*

$\bar{x}_i$ *is the mean for laboratory i;*

$\bar{\bar{x}}$ *is the mean of means.*

The confidence limits were obtained by calculation of the variance of the consensus value (mean of means) and reference to Student's-t distribution

$$\hat{V}(\bar{x}) = \frac{1}{p(p-1)} \sum_{i=1}^{p} (\bar{x}_i - \bar{x})^2$$

with degrees of freedom $(p-1)$.

$$Confidence\ limits = \bar{x} \pm t_{1-x/2}(p-1)(\hat{V}(\bar{x}))^{1/2}$$

where $t_{1-x/2}(p-1)$ is the 1-x/2 fractile of the t-distribution with (p-1) degrees of freedom.

The distribution of the values are assumed to be symmetrical about the mean in the calculation of the confidence limits.

The test for rejection of individual outliers from each laboratory data set was based on z scores (rejected if $|z_i| > 2.5$) computed from the robust estimators of location and scale, T and S, respectively, according to the formulae

$$S = 1.483 \; \underset{j=1,\dots,n}{median} |x_j - \underset{i=1,\dots,n}{median} (x_i)|$$

$$z_i = \frac{x_i - T}{S}$$

where
T is the median value in a data set;
S is the median of all absolute deviations from the sample median multiplied by 1.483, a correction factor to make the estimator consistent with the usual parameter of a normal distribution.

Summary of Results According to Analytical Method

COPPER

Method	No. of Laboratories	No. of Results	Median
Acid decomposition - titrimetric	3	30	3.02
Acid decomposition - atomic absorption	14	140	2.90
Borate fusion - X-ray fluorescence	2	14	3.10
Acid decomposition - ICP - MS	2	20	3.24
Acid decomposition - ICP - AES	1	17	2.94
Peroxide fusion - ICP - AES	3	30	2.84
Total	25	251	

LEAD

Method	No. of Laboratories	No. of Results	Median
Acid Decomposition - titrimetric	5	50	8.55
Acid decomposition - atomic absorption	10	110	8.60
Peroxide fusion - atomic absorption	2	14	8.68
Borate fusion - X-ray fluorescence	2	20	8.59
Peroxide fusion - ICP - AES	1	17	8.50
Acid decomposition - ICP - AES	2	20	8.75
Acid decomposition - ICP - MS	1	10	8.26
Total	23	231	

ZINC

Method	No. of Laboratories	No. of Results	Median
Acid decomposition - titrimetric	8	80	12.70
Acid decomposition - atomic absorption	9	90	12.70
Peroxide fusion - atomic absorption	1	10	12.82
Borate fusion - X-ray fluorescence	2	14	12.96
Peroxide fusion - ICP - AES	2	20	12.40
Acid decomposition - ICP - AES	1	17	13.10
Instrumental neutron activation	1	10	12.17
Total	24	241	

SILVER

Method	No. of Laboratories	No. of Results	Median
Acid decomposition - atomic absorption	12	120	570
Fire assay - gravimetric	1	10	515
Fire assay - atomic absorption	1	10	569
Peroxide fusion - atomic absorption	1	10	550
Acid decomposition - ICP - AES	2	27	570
Instrumental neutron activation	1	10	691
Total	18	187	

GOLD

Method	No. of Laboratories	No. of Results	Median
Fire assay - atomic absorption	8	72	2.58
Fire assay - gravimetric	1	10	2.70
Aqua regia - atomic absorption	5	49	2.60
Peroxide fusion - atomic absorption	1	10	2.58
Instrumental neutron activation	1	10	2.34
Total	16	151	

Uncertified Values

Approximate chemical composition	
Constituent	wt. %
SiO_2	50.0
TiO_2	0.10
Al_2O_3	1.54
Fe_2O_3	10.00
MnO	2.94
MgO	0.02
CaO	0.64
Na_2O	<0.01
K_2O	0.07
P_2O_5	0.01
Cu	2.95
Pb	8.54
Zn	12.68

Mineralogical composition	
Constituent	wt. %
Quartz	48
Sphalerite	22
Galena	10
Chalcopyrite	9
Spessartine	6
Pyrite	4
Ankerite	1

Participating Laboratories

Aberfoyle Resources Ltd., Hellyer, TAS
Amdel Laboratories, Thebarton, SA
Analabs, Welshpool, WA
Australian Assay Laboratories Group, Balcatta, WA
Australian Laboratory Services Pty Ltd., Stafford, QLD
Becquerel Laboratories, Lucas Heights, NSW
Broken Hill Associated Smelters, Port Pirie, SA
Genalysis Laboratory Services Pty Ltd, Maddington, WA

Mt Isa Mines Ltd., Mt Isa, QLD
Murchison Zinc Co Ltd, WA
Pasminco Metals - Sulphide Pty Ltd, Boolaroo, NSW
Pasminco Mining Rosebery, Rosebery, TAS
Pasminco Research Centre, Boolaroo, NSW
SGS Australia Pty Ltd, Queens Park, WA
Western Mining Corporation Ltd., Ballarat, VIC
Western Mining Corporation Ltd., Kalgoorlie, WA

Preparer and Supplier of the Reference Material

The OREAS 32 base metal sulphide ore reference material has been prepared and certified and is supplied by:

Ore Research & Exploration Pty Ltd
3 London Drive
Bayswater Vic 3153
AUSTRALIA

Telephone 61-(0)3-9762 1808
Facsimile   61-(0)3-9762 3808

It is sealed under nitrogen in laminated foil pouches in unit sizes of 5 and 50g. Both forms are supplied in lots of 10 and 2, respectively.

Intended Use

OREAS 32 is a reference material intended for the following:

i)   for the calibration of instruments used in the determination of the concentration of copper, lead, zinc, silver and gold;

ii)   for the verification of analytical methods for copper, lead, zinc, silver and gold;

iii)   for the preparation of secondary reference materials of similar composition.

iv)   as an arbitration sample for commercial transactions.

Stability and Storage Instructions

The sulphides contained in OREAS 32 are subject to oxidation on exposure to air. To ensure long term stability and minimal wastage the material has been equilibrated and sealed under nitrogen in laminated foil pouches in small unit sizes. The recommended values pertain to the date of certification and no responsibility is taken by Ore Research & Exploration Pty Ltd for changes occurring after receipt of goods. It is recommended that users minimise exposure to air when sampling and reseal opened foil pouches and store in dessicators, preferably under nitrogen gas.

Instructions for the Correct Use of the Reference Material

The recommended values for OREAS 32 contained herein refer to the concentration levels of copper, lead, zinc, silver and gold at the time of packaging. In this state a hygroscopic moisture content of 0.14% has been established by using AS2816 - 1992 (Annex A). If the reference material is dried by the user prior to analysis the recommended values should be corrected to the dry basis. It is also advised that the recommended drying procedure for materials susceptible to oxidation, detailed in the above reference, be strictly adhered to.

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.

Certifying Officer: Dr. Paul Hamlyn.

References

Hamlyn, P.R. (1992), Report on the preparation and certification of base metal sulphide ore reference material OREAS 32.

ISO Guide 35 (1985), Certification of reference materials - General and statistical principals.

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

AS 2816 - 1992, Copper, lead and zinc sulfide concentrates - Determination of hygroscopic moisture in the analysis sample - Gravimetric method.