CCRMP
Canadian Certified Reference Materials Project

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Certificate of Analysis

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CZN-4

Certified Reference Material for a Zinc Concentrate

Table 1 – CZN-4 Certified Values

Element	Units	Mean	Within-lab Standard Deviation	Between-labs Standard Deviation	95% Confidence Interval of Mean
Ag	µg/g	51.4	1.3	1.4	0.7
Al	%	0.0715	0.0027	0.0086	0.0063
As	%	0.0356	0.0009	0.0015	0.0011
Cd	%	0.2604	0.0046	0.0141	0.0074
Co	µg/g	93.5	3.3	6.4	3.7
Cu	%	0.403	0.011	0.010	0.006
Hg	µg/g	4.54	0.28	0.57	0.40
Pb	%	0.1861	0.0059	0.0085	0.0044
S	%	33.07	0.23	0.56	0.34
Se	µg/g	86.7	2.7	6.1	4.5
Si	%	0.295	0.013	0.026	0.019
Zn TITN	%	55.24	0.06	0.24	0.12

TITN = titration methods

Table 2 – CZN-4 Provisional Values

Analyte	Units	Mean	Within-lab Standard Deviation	Between-labs Standard Deviation	95% Confidence Interval of Mean
Ca*	%	0.0419	0.0021	0.0057	0.0061
Fe TITN	%	9.086	0.062	0.055	0.052
Fe non TITN	%	9.02	0.07	0.33	0.22
Mg*	%	0.0352	0.0010	0.0014	0.0014
Moisture	%	0.149	0.014	0.012	0.012
Zn non TITN	%	55.07	0.38	0.56	0.49

* *statistical analysis of the results warrants classification as provisional, despite only 6 sets of data for calcium and 7 data sets for magnesium*
Moisture was determined at 100-107°C for up to 24 hours on varying sample masses without use of nitrogen
TITN = titration methods
Non TITN = non titration methods

Table 3 – CZN-4 Informational Values

Element	Units	Mean	Number of accepted sets/values
Au	µg/g	0.04	3 / 15
Bi	µg/g	10	5 / 25
C	%	0.09	4 / 20
Cl	%	0.003	4 / 17
F	%	0.004	7 / 35
In	%	0.020	8 / 40
Mn	%	0.009	5 / 25
Ni	µg/g	16	7 / 35
Sb	µg/g	10	5 / 25
Sn	%	0.05	6 / 30

SOURCE
CZN-4 is a zinc sulphide flotation concentrate donated by Xstrata Copper Canada Division, Kidd Metallurgical Site, Timmins, Ontario, Canada. The raw material was obtained from the same source as its predecessor, CZN-3.

DESCRIPTION
The mineral species include: sphalerite (90.6%), pyrite (4.1%), pyrrhotite (3.3%), iron oxides (0.5%), quartz (0.5%), chalcopyrite (0.3%), various other silicates (0.2%), ankerite (0.1%), arsenopyrite, cassiterite, chlorite and galena (all at 0.1%).

INTENDED USE
CZN-4 is suitable for the analysis of zinc and various other elements at major, minor and trace levels in zinc concentrates. Examples of intended use include quality control and method development.

INSTRUCTIONS FOR USE

CZN-4 should be used "as is", without drying. The contents of the bottle should be thoroughly mixed before taking samples. The contents of the bottle should be exposed to air for the shortest time possible. Unused material should be stored under an inert gas in a desiccator, or in a new, heat-sealed laminated foil pouch. The values herein pertain to the material when produced. CANMET-MMSL is not responsible for changes occurring after shipment.

HANDLING INSTRUCTIONS

Normal safety precautions for handling fine particulate matter are suggested, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

METHOD OF PREPARATION

The raw material was dried at 32°C for 16 hours and sieved to remove the plus 74 µm fraction. The recovery from raw material to minus 75 µm fraction was 90%. The product was blended, and then bottled in 200-gram units. Each bottle was purged with nitrogen and sealed in a laminated polyethylene - foil pouch to prevent oxidation.

HOMOGENEITY

The homogeneity of the stock was investigated using fifteen bottles chosen according to a stratified random sampling scheme. Three splits were analyzed from each bottle. The splits were analyzed for zinc by the digestion of 0.25-gram sample using hydrochloric, nitric, hydrofluoric and perchloric acids. Various interfering elements were eliminated by precipitation and the use of complexing agents. A titration with ethylenediaminetetraacetate was used to determine the concentration of zinc. Corrections for lead and zinc were made based on the analysis of the filtrate by atomic absorption spectroscopy and fusion of the acid insoluble fraction. Samples of 0.25 grams from each split were analyzed for copper and lead using a four-acid digestion and inductively coupled plasma – atomic emission spectrometry. Use of a smaller sub-sample than specified above for these elements will invalidate the use of the certified values and associated parameters.

A one–way analysis of variance technique (ANOVA)[1] was used to assess the homogeneity of these elements. No significant between-bottle variation was observed for copper, lead and zinc.

CERTIFIED VALUES

Twenty-three (23) industrial, commercial and government laboratories participated in an interlaboratory measurement program using methods of their own choosing. The methods for zinc involved multi-acid digestions followed by iron separation, use of complexing agents and analysis of the filtrate by atomic absorption spectroscopy and fusion of the insoluble, ion exchange and solvent extraction. The determinations involved titrations with ethylenediaminetetraacetate and ferrocyanide, atomic absorption, and instrumental neutron activation analysis. Both fused pellet or fusion followed by X-ray fluorescence, as well as ISO 12739:2006 and ISO/TC 183 N 360 were used by some laboratories.

Other elements were determined by multi acid digestions, microwave digestion, fusion, fire assay (for gold and silver), flame atomic absorption spectroscopy, gravimetric analysis, inductively coupled plasma – optical emission spectroscopy, and instrumental neutron activation analysis. Some laboratories added bromine in order to destroy the organic residues.

Carbon was determined by combustion and infrared detection. Sulphur was determined in a similar manner and also by acid digestions, fusions, and sintering followed by gravimetric finish and inductively coupled plasma spectroscopy. Chlorine was separated from other elements by distillation, acid digestions and combustion. The determination was made using flame atomic absorption, coulometric titration, titration, photometry and ion specific electrode. Also, pressed powder pellets followed by X-ray fluorescence was used. Mercury was determined by various digestions and combustions, hydride generation, cold vapour atomic fluorescence spectroscopy, flameless atomic absorption spectroscopy and ASTM D 6722.

ANOVA was used to calculate the consensus values and other statistical parameters from the interlaboratory measurement program. Values are deemed to be certified if derived from 10 or more sets of data that meet CCRMP statistical criterion regarding the agreement of the results. Twelve (12) elements were certified (see Table 1).

Full details of all work, including the statistical analyses, the methods and the names of the participating laboratories are contained in the Certification Report. For more details on how to use reference material data to assess laboratory results, users are directed to ISO Guide 33:2000, pages 14-17, and the publication, "Assessment of laboratory proficiency using CCRMP reference materials", at www.ccrmp.ca.

UNCERTIFIED VALUES

The provisional value for iron by non titration methods (Table 2) was derived from 11 sets of data that did not fulfill the CCRMP statistical criterion required for certification. The data for iron by titration methods, moisture and zinc by non titration methods, all of which had less than 10 sets of data, fulfilled the statistical criteria for provisional status. Additionally, the statistical analysis of the data warranted provisional status for the 6 sets of data for calcium and 7 sets of data for magnesium. Informational values for 10 elements, shown in Table 3, were derived from the means of a minimum of 3 sets of data.

TRACEABILITY

The values quoted herein are based on the consensus values derived from the statistical analysis of the data from the interlaboratory measurement program, and the standards used by the individual laboratories. The report gives the available details.

CERTIFICATION HISTORY

CZN-4 is a new material.

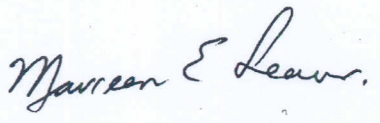
PERIOD OF VALIDITY

The certified values are valid until January 31, 2032. The stability of the material will be monitored every two years for the duration of the inventory. Updates will be published on the CCRMP web site.

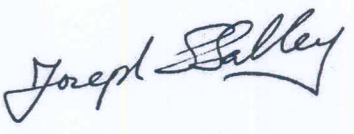
LEGAL NOTICE

CANMET-MMSL has prepared this reference material and statistically evaluated the analytical data of the interlaboratory measurement program to the best of its ability. The purchaser, by receipt hereof, releases and indemnifies CANMET-MMSL from and against all liability and costs arising out of the use of this material and information.

CERTIFYING OFFICERS



Maureen E. Leaver – CCRMP Coordinator



Joseph Salley – Data Processor

FOR FURTHER INFORMATION

The Certification Report is available free of charge upon request to:

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REFERENCES

1. Brownlee, K.A., Statistical Theory and Methodology in Science and Engineering; John-Wiley and Sons, Inc.; New York; 1960.