Certificate of Analysis

First issued: September 2023   Version: September 2023

CCU-1f

Certified Reference Material for a Copper Concentrate

Table 1 — CCU-1f Certified Values

The certified, provisional, and indicative values herein pertain to the material on an as-received basis. The exception is for copper which has values for both as received and dry-mass correction. Values for the other elements were generally derived from a variety of digestion, fusion and instrumental techniques. Specific techniques used are indicated with the element, i.e., titration (TITN), combustion (COMB), and two acid digestion (AD2), two and three acid digestions (AD2/3) and loss on ignition (LOI). Additional footnotes provide details of the analytical methods used to determine the values. For more detailed information please refer to the certification report.

Analyte	Units	Mean	Within-lab Standard Deviation	Between-labs Standard Deviation	95% Confidence Interval of Mean
Ag	µg/g	157.0	3.1	3.4	1.4
Al non AD2[a]	%	0.1203	0.0063	0.0076	0.0036
As	%	0.0821	0.0026	0.0040	0.0015
Au[b]	µg/g	19.08	0.81	0.81	0.43
Ca	%	0.140	0.006	0.014	0.006
Cd	µg/g	110.2	2.6	7.6	3.2
Co	µg/g	304.2	6.0	8.1	3.5
Cu as-received, classical[c]	%	23.33	0.09	0.15	0.08

Cont'd

Canada

Table 1 — CCU-1f Certified Values *Cont'd*

Analyte	Units	Mean	Within-lab Standard Deviation	Between-labs Standard Deviation	95% Confidence Interval of Mean
Cu dry-mass calculated correction, classical[d]	%	23.11	0.09	0.15	0.08
Cu as-received, instrumental[e]	%	23.31	0.30	0.35	0.15
Fe non TITN[e]	%	29.50	0.41	0.82	0.30
Hg[f]	µg/g	12.19	0.49	0.92	0.52
Mg non AD2[a]	%	0.383	0.006	0.024	0.010
Mn	µg/g	82.9	2.4	6.0	3.0
Pb	%	0.2095	0.0043	0.0073	0.0028
S COMB[g]	%	34.82	0.35	0.64	0.37
S non COMB	%	34.96	0.47	0.47	0.37
Sb	µg/g	85.5	2.9	8.9	4.5
SiO$_2$[h]	%	2.015	0.045	0.056	0.035
Te[f]	µg/g	49.9	2.5	8.8	4.9
Tl	µg/g	1.51	0.04	0.14	0.09
Zn	%	4.085	0.049	0.089	0.032

a data derived using digestion by two acids, hydrochloric and nitric acids, were excluded as method outliers based on statistical tests

b data were primarily derived by pre-concentration using fire assay with sample weights of 5–15 grams

c data using iodometric methods, ISO 10258:2018, titration methods, ISO 10469:2006, electrogravimetric methods and gravimetric methods were included only, based on statistical tests

d calculated value based on data indicated for copper as-received by classical methods with a moisture correction

e data using primarily instrumental techniques such as flame atomic absorption spectroscopy, X-ray fluorescence spectrometry, inductively coupled plasma optical emission spectroscopy and mass spectrometry, were included based on statistical tests

f data were derived primarily from various acid digestions

g data from combustion apparatus only were included, based on statistical tests

h data were derived primarily from various types of fusions

Table 2 — CCU-1f Provisional Values

Analyte	Units	Mean	Within-lab Standard Deviation	Between-labs Standard Deviation	95% Confidence Interval of Mean
Bi[a]	µg/g	0.649	0.041	0.050	0.041
Ce[a,b]	µg/g	0.80	0.05	0.12	0.11
Fe TITN[b]	%	29.66	0.10	0.28	0.30
Ga[a,b]	µg/g	3.39	0.10	0.26	0.24
In[a,b]	µg/g	5.71	0.18	0.46	0.49
K[b]	%	0.0161	0.0020	0.0032	0.0031
LOI[c]	%	19.15	0.29	0.77	0.61
Mo[d,e]	µg/g	11.6	0.6	3.7	2.2
Ni[f]	µg/g	19.2	0.8	1.4	1.1
Se[g]	µg/g	211	9	16	13
Ti	µg/g	52.8	2.2	4.8	4.1
W[a,b]	µg/g	1.12	0.14	0.14	0.14

a data were derived by acid digestion only

b statistical analysis of the data warrants classification as provisional despite only six or seven sets of data

c samples of 1 to 3 grams were ignited for 1 to 12 hours at 700 to 1000 degrees Celsius

d there is not enough data to demonstrate whether certain conditions using only nitric and hydrochloric acids can result in an incomplete digestion

e data were classified as provisional since the between-laboratory standard deviation is approximately 30% of the mean

f data using digestion by various mixtures of 3 and 4 acids only were included, based on statistical tests

g data were derived by four acid and complete digestion only, based on statistical tests

Table 3 — CCU-1f Indicative Values (semi-quantitative only)

Analyte	Units	Mean	No. Accepted Laboratories/Values
Al AD2[a]	%	0.07	4/20
Ba	µg/g	7	7/34
C[b]	%	0.06	9/44
Cr[c]	µg/g	7	8/40
F	µg/g	80	7/33
Ge[c]	µg/g	0.8	6/30
Li[c]	µg/g	0.4	7/34
Mg AD2[a]	%	0.07	4/20
Moisture[d]	%	0.96	6/30
Na	%	0.02	9/43
Ni AD2[a]	µg/g	13	6/30
P[c]	µg/g	13	7/35
Rb[c]	µg/g	0.3	7/35
Re[c]	µg/g	0.005	7/33
Sc[c]	µg/g	0.5	6/30
Se AD2/3[e]	µg/g	200	6/29
Sn[c]	µg/g	9	8/39
Sr[c]	µg/g	2	8/40
U[c]	µg/g	0.4	8/40
V	µg/g	3	10/50
Y[c]	µg/g	0.8	7/35

a data were derived by digestion using nitric and hydrochloric acids only

b data were derived by combustion, using samples of 1 to 3 grams, ignited for 1 to 12 hours at 700 to 1000 degrees Celsius

c data were derived by digestion with various combinations of acids only

d data were derived from samples of 1 to 10 grams dried for 10 minutes to 24 hours at 105 degrees Celsius

e data using digestion by various mixtures of 2 and 3 acids were included, based on statistical tests

SOURCE
CCU-1f is a copper concentrate donated by Hudbay Minerals Inc., from the mill in Flin Flon, Manitoba, Canada.

DESCRIPTION
The mineral species include: chalcopyrite (74.19%), pyrite (15.17%), sphalerite (3.64), Fe-Cu sulphides—mixture (1.17), enstatite (0.77%), other silicates (0.41%), Fe-oxide (0.33%), quartz (0.20%), gypsum (0.17%), chlorite–clinochlore (0.16%), galena (0.16%), aluminosilicates—mixture (0.07%), fayalite (0.04%), albite (0.04%), muscovite (0.02%), epidote (0.01%), unclassified (3.44%).

INTENDED USE
CCU-1f is suitable for the analysis of copper concentrates for copper and other elements at concentrations ranging from major, minor to trace levels. Examples of intended use include quality control and method development.

INSTRUCTIONS FOR USE
CCU-1f should be used "as is" without drying for all elements. The contents of the bottle should be thoroughly mixed before taking samples. The contents of the bottle should be exposed to ambient 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 under an inert gas. Changes in the moisture content, caused by the adsorption or loss of moisture, can significantly affect the concentration of copper.

For applications related to commercial exchange, copper values are generally reported on a dry-mass basis. Separate portions for both the moisture determination and the copper determination should be taken at the same time. ISO 9599:2015, Copper, lead, zinc and nickel sulfide concentrates - Determination of hygroscopic moisture content of the analysis sample - Gravimetric method, or a similar standard, describes the procedure.

The values herein pertain to the date when issued. CanmetMINING 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 for 24–72 hours at 32°C, milled and sieved. The recovery of the material less than 75 μm (- 200 mesh fraction) was 81%. The product was blended and bottled in 200-gram units. This is the only size that is available. Each bottle was purged with nitrogen and sealed in a laminated aluminum 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 subsamples per bottle were analyzed for copper using electrodeposition with correction for co-plated impurities and residual copper in solution. Gold in triplicate samples of five grams each per bottle, dried for one hour at 105°C, was analysed by pre-concentration using lead fire assay and determined using gravimetric analysis. The homogeneity of the stock for lead and zinc was investigated using another set of 15 bottles selected according to a stratified random sampling scheme. Three subsamples from each bottle were analyzed. Each sub-sample of 0.5 grams was digested with hydrochloric,

nitric, hydrofluoric, and boric acids followed by inductively coupled plasma optical emission spectrometry and mass spectrometry.

A one–way analysis of variance technique (ANOVA)[1] and statistical analyses were used to assess the homogeneity of these elements. No significant between-bottles variation was observed for all elements.

Use of a smaller subsample than specified above will invalidate the use of the certified values and associated parameters.

CERTIFIED VALUES

Twenty-one industrial, and commercial laboratories participated in an interlaboratory measurement program using methods of their own choice.

Copper was determined by (i) iodometric and various titration methods, ISO 10258:2018, electrogravimetric analysis, gravimetric methods, and ISO 10469:2006, (ii) digestion using a variety of acids and fusion followed by flame atomic absorption spectroscopy, inductively couple plasma optical emission spectroscopy and inductively coupled plasma mass spectrometry, and (iii) fusion followed by X-ray fluorescence spectrometry.

Gold was determined primarily by fire assay with sample weights ranging from 5–15 grams.

Carbon was determined using combustion followed by infrared spectrometry.

Iron was determined by (i) titrimetric methods, (ii) digestion using a variety of acids and fusion followed by flame absorption spectroscopy, inductively couple plasma optical emission spectroscopy, inductively coupled plasma mass spectrometry, and (iii) fusion followed by X-ray fluorescence spectrometry.

Loss on ignition values were determined on samples from one to three grams ignited for one to 12 hours at 700 to 1000°C.

Moisture was determined on samples ranging from one to 10 grams, dried from 10 minutes to 24 hours at 105°C.

Sulphur was determined using (i) combustion followed by infrared spectrometry; and (ii) digestion with various combinations of acids or fusion followed by gravimetric analysis, inductively coupled plasma optical emission spectroscopy or (iii) fusion followed by X-ray fluorescence spectrometry.

Methods for the determination of various other elements included (i) digestion with variety of acids on a hot plate or using a microwave oven, or various types of fusions, followed by flame atomic absorption spectroscopy, inductively coupled plasma optical emission spectroscopy and inductively coupled plasma mass spectrometry, or (ii) pressed powder, fused pellet or fusion followed by X-ray fluorescence spectrometry.

ANOVA was used to calculate the consensus values and other statistical parameters from the data from the interlaboratory measurement program. Values are deemed to be certified if derived from 10 or more sets of data that meet CCRMP's statistical criterion regarding the agreement of the results. Twenty-two means 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 33:2017,

and the publication, "Assessment of laboratory proficiency using CCRMP reference materials", available from the CCRMP website.

UNCERTIFIED VALUES
The mean of each of six analytes (Table 2) was derived from eight or nine sets of data that fulfill the CCRMP statistical criterion regarding agreement; or 10 or more sets of data that do not fulfill the CCRMP statistical criteria required for certification. Additionally, the statistical analysis of the six or seven sets of data fulfilled the criteria for provisional status for cerium, gallium, indium, and tungsten by various acid digestions only, iron by titration, and potassium by acid digestion and fusion. Indicative values for 21 elements, shown in Table 3, were derived from the means of a minimum of 4 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
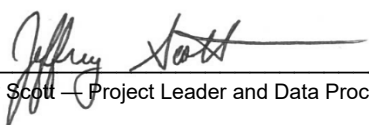CCU-1f was released as a new material in September 2023.

PERIOD OF VALIDITY
The certified values are valid until September 30, 2043. The stability of the material will be monitored every two years for the duration of the inventory. Updates will be published on the CCRMP website.
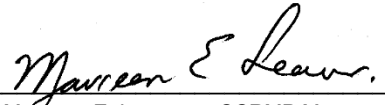
LEGAL NOTICE
CanmetMINING has prepared this reference material and statistically evaluated the analytical data of the interlaboratory measurement program to the best of its ability. The purchaser, by receipt hereof, releases and indemnifies CanmetMINING from and against all liability and costs arising out of the use of this material and information.

CERTIFYING OFFICERS

Jeffrey Scott — Project Leader and Data Processor

Maureen E. Leaver — CCRMP Manager

FOR FURTHER INFORMATION
CCU-1f was prepared in consideration of the principles in ISO Guides 30, 31, 33 and 35, and ISO 17034. 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.