

This document was produced  
by scanning the original publication.

Ce document est le produit d'une  
numérisation par balayage  
de la publication originale.

**CANADA**

**DEPARTMENT OF MINES AND TECHNICAL SURVEYS**

**OTTAWA**

**MINES BRANCH INVESTIGATION REPORT IR 61-80**

**QUANTITATIVE DETERMINATION BY THE  
STALLWOOD AIR-JET DC ARC TECHNIQUE**

**2. TRACE IMPURITIES IN HIGH PURITY COPPER**

by

**K. BHASKARA RAO & A. H. GILLIESON**

**MINERAL SCIENCES DIVISION**

**COPY NO.**

**4**

**JULY 12, 1961**

Mines Branch Investigation Report IR 61-80

QUANTITATIVE DETERMINATION BY THE  
STALLWOOD AIR-JET DC ARC TECHNIQUE  
2. TRACE IMPURITIES IN HIGH PURITY COPPER

by

K. Bhaskara Rao\* and A.H. Gillieson\*\*

- - - -

SUMMARY OF RESULTS

Trace impurities in high  
purity copper metal can be adequately  
determined by a quantitative modification  
of the normal Stallwood Air-Jet dc Arc  
Technique.

---

\*Chief Chemist, Hindustan Aircraft Ltd., Bangalore, India. At  
present National Research Council of Canada Post-doctorate  
Research Fellow attached to the Mines Branch.

\*\*Senior Scientific Officer, Analytical Chemistry Subdivision,  
Mineral Sciences Division, Mines Branch, Department of Mines  
and Technical Surveys, Ottawa, Canada.

## INTRODUCTION

The present investigation was undertaken to evaluate the applicability of the Stallwood Air-Jet dc Arc Technique(1, 2, 3, 4) to the determination of impurities in a high purity copper sample from Canadian Copper Refiners Ltd., and in the same material after treatment, submitted by R. Thompson, Physical Metallurgy Division, Mines Branch.

## OUTLINE OF THE METHOD

Spectra of standards and samples were obtained under similar conditions using the normal Stallwood procedure. The intensities of the internal standard line and impurity lines were measured by the Sturrock Cathode Ray Densitometer. Working curves were prepared for the impurity elements by plotting the intensity ratios of the analytical line pairs against concentration on log-log graph paper and the concentrations of impurity elements in the samples were read from the curves.

## APPARATUS AND MATERIALS

### Excitation Source

Excitation was obtained from an A.R.L. dc Arc Source  
Unit Type No. 02825 A.

### Spectrograph

Baird 3 metre grating spectrograph having a reciprocal  
dispersion of 5.5 Å/mm.

### Microphotometer

The intensity of spectrum lines was measured by the  
Sturrock Cathode Ray Densitometer.

### Photographic Processing Equipment

The plates were developed in a thermostatically  
controlled A.R.L. developing machine and dried on the A.R.L.  
plate dryer.

### Sample Preparation Equipment

The samples were filed by a high speed motor-driven  
steel burr.

### Standards

Johnson and Matthey spectrographic copper standards  
(CA, CB and CC series) were used as standards for preparing the  
working curves. The composition of these samples is given in  
Table 1.

TABLE 1

Composition of Cu Standards - (Johnson, Matthey)

<u>Alloy No.</u>	<u>SERIES CA</u>						
	<u>Sb</u>	<u>Bi</u>	<u>Cr</u>	<u>Ga</u>	<u>Pb</u>	<u>Ag</u>	<u>Sn</u>
CA0	0.048	0.062	0.046	0.033	0.045	0.049	0.036
CA1	0.019	0.025	0.018	0.013	0.018	0.02	0.015
CA2	0.01	0.012	0.009	0.006	0.009	0.01	0.007
CA3	0.005	0.006	0.0045	0.003	0.0045	0.005	0.0035
CA4	0.002	0.0025	0.0018	0.0013	0.0018	0.0021	0.0015
CA5	0.001	0.00125	0.0009	0.0006	0.0008	0.0011	0.00065
CA6	0.007	0.00064	0.00045	0.00033	0.00045	0.0006	0.00035
CA7	0.00015	0.00027	0.0003	0.0003	0.0003	0.0003	0.00015
CA8	0.0001	0.00014	0.0001	0.0002	0.0003	0.0002	0.000075

SERIES CB

<u>Alloy No.</u>	<u>Co</u>	<u>Fe</u>	<u>Mn</u>	<u>Ni</u>	<u>Si</u>
CB0	0.052	0.023	0.046	0.033	0.049
CB1	0.02	0.011	0.018	0.015	0.02
CB2	0.01	0.005	0.009	0.01	0.016
CB3	0.0052	0.0025	0.0035	0.005	0.004
CB4	0.002	0.002	0.0018	0.0015	0.002
CB5	0.0011	0.0009	0.0009	0.001	0.0011
CB6	0.0005	0.001	0.00022	0.00035	(0.0005)
CB7	(0.0002)	0.001	0.00018	0.001	(0.0002)
CB8	(0.0001)	0.0004	0.00004	0.0002	(0.0001)

(cont' d)

TABLE 1 (cont' d)

SERIES CC

<u>Alloy</u> <u>No.</u>	<u>As</u>	<u>Be</u>	<u>P</u>	<u>Te</u>	<u>Zn</u>
CC0	0.14	0.04	0.048	0.031	0.066
CC1	0.056	0.012	0.011	0.0125	0.023
CC2	0.026	0.010	0.0096	0.0062	0.013
CC3	0.014	0.004	0.0035	0.0015	0.006
CC4	0.0056	0.002	0.0018	0.0012	0.0025
CC5	0.0027	0.0006	0.001	0.0009	0.0015

---

### Electrodes

The upper electrode was a National Carbon Co. high purity graphite rod L 3803, 1/8 in. diameter with a pointed end. The lower electrode was a 1/8 in. diameter graphite rod with a 0.086 in. diameter hole drilled to a depth of 1 in.

### Photographic Materials

Eastman Kodak Spectrum Analysis No. 2 plates were used for recording the spectra. Eastman Kodak D-19 developer and F-10 fixer were employed for developing the plates.

## EXPERIMENTAL DETAILS

### Electrode System

10 mg of the prepared copper filings and 40 mg of National Carbon Co. SP-1 graphite powder (100 mesh) were weighed in a rhodium-plated dish, mixed well with a graphite rod and transferred to the graphite electrode cup by means of a rhodium-plated funnel. The electrode was sealed on the top with a small drop of celluloid solution and was then placed in the lower, positive electrode holder. The pointed electrode was placed in the upper, negative electrode holder.

### Excitation, Exposure and Photographic Processing

The excitation of the electrodes, the recording of the spectra and the processing of the photographic plates were done under the conditions stated below.

Conditions of Excitation and Exposure

Source of excitation:	dc arc
Arc current:	6 amperes
Line voltage:	200 volts
Spectral region:	2200-3500 A
Slit width:	0.025 mm
Stepped sector:	1-10-100% rotary
Separation of electrodes:	2 mm (continually adjusted by means of back-projection screen arrangement)
Electrode-holders:	water cooled
Pressure of the air jet:	3 in. of mercury
Arc preburn:	none
Arc exposure period:	complete burning indicated: (1) by the change in the colour of the arc and shape of electrodes and (2) by the change in the noise of the arc due to increase in the rate of burning.

Conditions of Photographic Processing

Emulsion:	Eastman Kodak S.A. No. 2 plates
Developing:	Eastman Kodak D-19, rocked for 6 min at 20°C
Stop bath:	water, rocked for 15 sec
Fixing:	Eastman Kodak F-10, rocked for 10 min



Washing:	running water for 30 min
Drying:	stream of hot air from A.R.L. plate dryer.

### Photometry

The intensities of the internal standard line and impurity lines were measured on the Sturrock Cathode Ray Densitometer. The wavelength of the analytical line chosen for each impurity element is given in Table 2.

### Working Curves

Working curves were prepared for each impurity element by plotting the concentration against the ratio of the intensities of the analytical line and the internal standard line on log-log (3 x 2 cycles) graph paper.

### Lower Limits of Determination of Impurity Elements in Copper

The lower concentration limits that can be satisfactorily determined by this procedure were evaluated for all impurity elements detected in the copper standards and are reported in Table 2.

### Determination of Impurities in the P.M.D. Samples

The percentage of the impurity elements in the samples submitted are reported in Table 3. The first sample represents the material as received from Canadian Copper Refiners Ltd.

TABLE 2

Analytical Lines and Limits of Detection

Element	Wavelength in A	Lower Limit of Detection Per cent
Copper	3108.6	Principal Constituent. Internal Standard
Antimony	2598.06	0.004
Bismuth	3067.72	0.001
Chromium	2835.6	0.001
Gallium	2943.7	0.0005
Lead	2833.07	0.004
Silver	3382.9	0.0005
Tin	2839.99	0.0006
Cobalt	3453.5	0.002
Iron	3020.64	0.0004
Manganese	2794.82	0.0001
Nickel	3414.8	0.001
Silicon	2881.58	0.0005
Arsenic	2349.84	0.005
Beryllium	3130.4	0.001
Phosphorus	2535.6	0.01
Tellurium	2385.76	0.002
Zinc	3302.59	0.02 by visual comparison

TABLE 3

Impurity Elements in P.M.D. Copper Samples

Description of Samples	Per cent								
	Fe	Mn	Si	Sn	Sb	As	Ni	Pb	Zn
ICCR Ingot 1	0.0015 (0.0025)	<0.0001 -	- -	0.0007 -	0.004 (0.001)	0.013 (0.0003)	<0.001 (0.0025)	- (0.002)	N.D. <0.02
582-1	0.02	"	-	0.012	0.031	-	"	-	"
593A-5	0.03	"	-	0.018	0.05	-	"	-	"
GF-5-4-17	0.01	"	-	0.0006	0.02	-	"	-	"
GF-4-2-14	0.04	"	-	0.0009	0.05	-	"	-	"
GF-2-4-8	0.02	0.0001	-	0.0045	0.03	-	0.002	-	"
GF-4-3-15	0.07	0.0009	-	0.0008	0.09	-	0.002	-	"
GF-3-3-11	0.02	0.0008	-	0.0034	0.02	-	0.002	-	"
S-351	0.03	0.0036	0.04	0.014	0.04	-	0.007	0.006	"

N.D. = not detected

The bracketted figures in the second line are the impurity concentrations quoted by the supplier for this type of material.

## CONCLUSIONS

The results of this investigation show that the normal Stallwood dc Arc Technique can be employed satisfactorily for the determination of trace impurities in high purity copper. Since the procedure does not require any chemical treatment of the metallic filings, the sample preparation is simple and the chances of contamination during the sample preparation are minimized.

## REFERENCES

1. B.J. Stallwood, "Development of a General Method for the Spectrographic Analysis of Powder Samples" Thesis, University of Toronto (1951).
2. B.J. Stallwood, J. Opt. Soc. Am. 44, 171 (1954).
3. R.F. Sturrock and F.A. Lang, "Semi-Quantitative and Quantitative Spectrographic Analysis with the Stallwood Air-Jet Source", 1st Ottawa Symposium on Applied Spectroscopy, Mines Branch, Ottawa, September 20, 1954.
4. A.H. Gillieson, "Quantitative Determination by the Stallwood Air-Jet dc Arc Technique. Part I. Trace Impurities in Titanium Oxide", Mines Branch Investigation Report IR 61-48, Department of Mines and Technical Surveys, Ottawa (1961).

- - - -

KBR:AHG/DV