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**ANALYSIS OF C.A.A.S. COPPER STANDARDS  
BY ATOMIC ABSORPTION  
SPECTROPHOTOMETRY**

by

**J. C. HOLE AND D.J. CHARETTE**

**MINERAL SCIENCES DIVISION**

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SUMMARY

The trace elements iron, lead, nickel, silver, zinc, magnesium and manganese have been determined in each of five high-purity copper standards, using the technique of atomic absorption spectrophotometry. A brief description of the method used is given, and the results tabulated and discussed.

The application of atomic absorption to highly accurate determinations of the small amounts of elements in the standards has also been discussed.

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## INTRODUCTION

The Non-Ferrous Standards Committee of the Canadian Association for Applied Spectroscopy has prepared a series of five high-purity copper standards. The Committee intends to certify these standards for several elements occurring in trace amounts. Samples from these standards have been distributed to a number of laboratories. It was requested that the Mineral Sciences Division analyse these standards by the technique of atomic absorption spectrophotometry.

It was decided to determine seven elements, iron, lead, nickel, silver, zinc, magnesium and manganese, in each of the five standards.

The amounts of the trace elements present were well below the usual working range of atomic absorption, so the analysis could not be carried out directly on the samples. Also, the effect of the matrix and the other elements present on the determination of the seven elements was not known.

A determination following separation of the major component, copper, and subsequent concentration of the remaining elements, would still require knowledge of the effect of the trace elements on each other, and would also introduce a large amount of handling of the samples, thus increasing the possibility of experimental error.

To eliminate these difficulties, the technique of standard addition was chosen. This technique involves a minimum of manipulation, increases the amount of an element present to a range suitable for atomic absorption analysis, and also compensates for the effect of the matrix and the other elements present. However, it must be realized that the standard addition technique places all of the errors inherent in the whole analytical method onto the small net result calculated for the sample itself.

## APPARATUS

A Techtron Model AA-3 atomic absorption spectrophotometer equipped with a hollow cathode lamp for each element determined was used, in conjunction with a Photovolt Varicord Model 43 recorder.

## METHOD

Approximately 10 g of each sample were rinsed in 1:2 HCl with a few drops of concentrated  $\text{HNO}_3$  added to remove surface contamination, washed with water and then with acetone, and weighed. The samples were then dissolved in either 100 ml of 1:1  $\text{HNO}_3$ , or in a mixture of 80 ml of 1:1  $\text{HNO}_3$  and 20 ml of concentrated HCl. The use of either acid system led to similar results, except in the case of silver. When silver was being determined, samples dissolved in 1:1  $\text{HNO}_3$  only were used.

After dissolution, the samples were transferred to 250 ml volumetric flasks and diluted to volume with water. A 25 ml aliquot of each of these samples was added to each of a series of three 50 ml volumetric flasks.

For each sample series, different amounts of a standard solution of an element being determined were added to the three flasks, and the solutions diluted to volume. In some cases, standard additions of more than one element were added to the same sample series.

The absorbance of each of the elements added to the series of flasks was measured, and the results used to calculate the concentration in parts per million of that element in the original copper sample.

The reagents were found to contribute a maximum of 0.1 ppm of the element being determined in the copper standards.

Distilled and de-ionized water was used throughout.

## RESULTS

A total of 280 independent determinations were completed, and the results are listed in Table 1. For each element in each standard sample, Table 2 shows the mean ( $\bar{x}$ ) of all eight determinations, the standard deviation (s), and the coefficient of variation (c.v.).

Chauvenet's criterion (1) was successively applied to the data in Table 1, and the results marked with an asterisk were rejected. The means, standard deviations, and coefficients of variation were then recalculated and are shown in Table 3.

TABLE 1

Determination of Trace Elements in Copper Standards

(all figures in ppm)

Element	#1554 Bar Mark 22 Lot #1	#1555 Bar Mark 1 Lot #2	#1556 Bar Mark 2 Lot #3	#1557 Bar Mark 3 Lot #4	#1558 Bar Mark 4 Lot #5
Fe	18, 8, 10 4, 7, 1 11, 9	50, 32, 30 26, 31, 45 30, 28	43, 13, 28 25, 39, 21 24, 27	51, 46, 30 30, 29, 11* 36, 40	58, 55, 54 54, 61, 68 60, 64
Pb	3, 17, 12 12, 31*, 10 15, 6	78, 89*, 70 79, 73, 73 40*, 75	21, 25, 10 26, 26, 17 22, 16	12, 16, 19 14, 28, 15 35, 18	36, 27, 28 31, 25, 27 25, 38
Ni	3, 16, 9 3, 2, 6 7, 6	19, 18, 21 18, 15, 23 19, 14	1, 4, 6 5, 5, 5 16*, 3	56, 54, 49 33*, 54, 61 67, 61	20, 22, 19 25, 21, 30 27, 26
Ag	4*, 9, 11 12, 15, 18*, 16, 16	13, 20, 18 41, 27, 30 27, 30	20, 14, 14 19, 16, 21 24, 21	18, 12, 18 26, 21, 24 25, 21	22, 23, 28 44*, 30, 31 35, 29
Zn	9, 18, 11 10, 12, 11 11, 12	37, 43, 52 46, 41, 41 45, 45	18, 20, 26 25, 29, 21 26, 24	14, 25, 19 34*, 17, 21 23, 18	42*, 53, 49 49, 49, 51 49, 51
Mg	0.1, 0.9, 0.9 0.5, 1.1, 0.6 1.1, 0.5	1.3, 1.7, 1.3 2.0, 1.0, 1.1 1.9, 2.0	0.4, 1.3, 1.6 1.0, 0.9, 1.0 1.0, 0.9	0.1, 0.7, 0.9 1.0, 2.5, 1.1 2.1, 0.5	0.8, 1.1, 1.0 1.5, 0.9, 1.5 1.5, 1.0
Mn	0.6, 0.7, 0.8 1.5, 3.9, 5.7 3.3, 6.1	2.8, 0.6, 0.7 6.4, 3.8, 5.9 7.0, 6.0	0.6, 0.6, 0.7 6.3, 0.9, 5.8 7.5, 6.6	1.2, 0.6, 0.7 5.7, 6.6, 7.4 7.3, 6.9	2.4, 2.5, 3.6 5.0, 5.5, 5.5 8.1, 8.5

\* denotes results rejected by Chauvenet's criterion.

TABLE 2

Summary of Determinations in Table 1

(Chauvenet's criterion not applied)

Element	Data	#1554 Bar Mark 22 Lot #1	#1555 Bar Mark 1 Lot #2	#1556 Bar Mark 2 Lot #3	#1557 Bar Mark 3 Lot #4	#1558 Bar Mark 4 Lot #5
Fe	$\bar{x}$ (ppm) s c.v. (%)	9 5 55	34 9 26	28 10 35	34 12 35	59 5 9
Pb	$\bar{x}$ s c.v.	13 8 61	72 14 19	20 6 30	20 8 40	30 5 17
Ni	$\bar{x}$ s c.v.	7 5 72	18 3 17	6 4 67	54 10 19	24 4 17
Ag	$\bar{x}$ s c.v.	10 3 30	26 9 35	19 4 21	21 5 24	30 7 23
Zn	$\bar{x}$ s c.v.	12 3 25	44 4 9	24 4 17	21 6 29	49 3 6
Mg	$\bar{x}$ s c.v.	0.7 0.3 43	1.5 0.4 27	1.0 0.3 30	1.1 0.8 73	1.2 0.3 25
Mn	$\bar{x}$ s c.v.	2.8 2.3 82	4.2 2.6 62	3.6 3.2 89	4.6 3.1 67	5.1 2.3 45

TABLE 3

Summary of Determinations in Table 1

(Chauvenet's criterion applied)

Element	Data	#1554 Bar Mark 22 Lot #1	#1555 Bar Mark 1 Lot #2	#1556 Bar Mark 2 Lot #3	#1557 Bar Mark 3 Lot #4	#1558 Bar Mark 4 Lot #5
Fe	$\bar{x}$ (ppm)	9	34	28	37	59
	s (ppm)	5	9	10	9	5
	c.v. (%)	55	26	35	24	9
Pb	$\bar{x}$	11	75	20	20	30
	s	5	3	6	8	5
	c.v.	45	4	30	40	17
Ni	$\bar{x}$	7	18	4	57	24
	s	5	3	2	6	4
	c.v.	72	17	50	11	17
Ag	$\bar{x}$	13	26	19	21	28
	s	3	9	4	5	5
	c.v.	23	35	21	24	18
Zn	$\bar{x}$	12	44	24	20	50
	s	3	4	4	4	2
	c.v.	25	9	17	20	4
Mg	$\bar{x}$	0.7	1.5	1.0	1.1	1.2
	s	0.3	0.4	0.3	0.8	0.3
	c.v.	43	27	30	73	25
Mn	$\bar{x}$	2.8	4.2	3.6	4.6	5.1
	s	2.3	2.6	3.2	3.1	2.3
	c.v.	82	62	89	67	45

## DISCUSSION

Since each determination of an element was carried out on a separate portion of a sample, small deviations from homogeneity of the sample may be apparent because of the small amounts of the elements present. A comparison of the coefficients of variation in Table 3 for sample #1554 with those for the other four samples indicates that this sample is less homogeneous than the others. This confirms the results of an independent homogeneity test of the samples (2).

The precision of the experimental method used in this investigation is affected by the usual experimental errors, by errors arising from the standard addition technique, and especially by the use of atomic absorption.

Instability occurs in atomic absorption, caused mainly by the flame and the particular hollow cathode lamp being used, and this in turn will cause a wide variation in results (i.e., a high standard deviation) which is serious at the low analytical ranges involved here. A high value of the standard deviation will result in an increasingly high value of the coefficient of variation as the amount of element present decreases.

On the other hand, the sensitivity of the determination of different elements by atomic absorption varies widely. The determination of elements of greater sensitivity will result in lower values of the standard deviation. In this case, zinc and magnesium are known to be more sensitive than the other five elements.

These concepts are illustrated by the data in Table 3. In the case of iron, lead, nickel and silver, the instability of atomic absorption results in relatively large standard deviations; these in turn cause relatively high coefficients of variation at the analytical level of these elements.

The manganese determinations result in standard deviations comparable to those for iron, lead, nickel and silver. However, the manganese content of the samples is lower than for these four elements, and consequently the coefficients of variation are higher.

In the case of the more sensitive element magnesium, the standard deviations are lower than for the elements iron, lead, nickel, silver and manganese. However, the low amounts of magnesium present give rise to coefficients of variation comparable to those for these five elements.



Similarly the standard deviations are lower for zinc than for iron, lead, nickel, silver and manganese. In this case the analytical levels are comparable to iron, lead, nickel and silver, so lower coefficients of variation are obtained than for these four elements.

### CONCLUSIONS

The five copper standards have been analysed for seven trace elements and the results are shown in Tables 1 to 3. It has been shown that sample #1554 is not as homogeneous as the other four.

The magnitude of the coefficients of variation of the analytical results indicates that the analytical method and instrumentation employed in this investigation is not suitable for highly accurate determinations of the small amounts of the seven elements present in the copper standards. The reasons for this unsuitability have been discussed.

### REFERENCES

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