

R. K. H. Chan,¹ A.M. and A. H. Li,¹ B.A.Sc.

Comparison of Single Stranded Copper Wires by Spectrochemical Analysis Using Copper Fluoride as a Carrier

In an earlier report [1] a method was outlined for the comparison of single-stranded copper wires by nondestructive neutron activation analysis. This method gives both precise and accurate results but can be time consuming and expensive when a large number of copper wires are to be compared. Our laboratory has been seeking other speedier means of comparing copper wires to complement the neutron activation method even at some sacrifice in sensitivity, precision, and accuracy.

In a recent theft, about one mile in length of telegraphic copper wires was stripped from poles spaced approximately 150 feet apart. A large number of coils of copper wires comprised of four bare single strands twined together were recovered in a scrapyard. Each of the four strands was number 9 gage and approximately 150 feet in length. All the wires were covered with a heavy coat of greenish corrosion product.

Remnants of wires from several inches to 1½ ft long were left on most of the poles at the scene of the theft. Most poles contained remnants of four strands but a few had only two or three. All were similar in appearance to the recovered wires.

Three coils of four strands each recovered from the scrapyard together with wire remnants from 29 consecutive poles were sent to this laboratory for comparison. On close examination, several strands in two of the three coils were found to be made up of two different strands joined together by a copper connector. Only one coil was free from this complication; hence, it was used for comparison with the large number of wire remnants. In view of the large number of comparisons involved, neutron activation analysis was deemed impractical; and it was decided to employ the emission spectrographic method.

Tymchuk, Mykytiuk and Russell [2] reported a technique of spectrochemical analysis of trace impurities in high purity copper using copper fluoride as a carrier. Test runs were carried out on standards using similar operating conditions and results were found to be satisfactory. Hence, this method was applied for the analysis of copper wires except for the following approximation in the handling of data.

Approximation in Data Handling

In spectrographic work, the relationship between the intensity of a spectral line of an element and the concentration is expressed empirically by the Scheibe-Lomakin equation:

$$I = KC^n \quad (1)$$

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¹ Chemistry Section, The Centre of Forensic Sciences, Toronto, Ontario, Canada.

where I = intensity of the spectral line

K = proportional constant, depending upon the excitation of the spectral line and temperature of the arc

C = concentration of the element

n = self-absorption of the spectral line

Assume $n = 1$, a good approximation based on our test runs, then the following relationship follows:

$$\frac{I_{\text{unknown}}}{I_{\text{standard}}} = \frac{C_{\text{unknown}}}{C_{\text{standard}}} \quad (2)$$

Equation 2 was used throughout this work. The above approximation is in essence another version of the single point working curve method described by Ahrens and Taylor [3]. They mentioned that this approximation was only suitable for the analysis of unknowns over a limited range of concentration. This is, of course, true if the actual working curve differs greatly from 45 deg or n differs greatly from 1. In our preliminary study, n is close to 1; hence, this approximation should apply to a greater range of concentrations.

In forensic science work it is not as important to determine the true concentrations of the trace elements of a copper wire sample as to show whether one sample matches another sample even on arbitrary concentration scales. If n is not close to 1, the C_{unknown} in Eq 2 can be regarded as apparent rather than true concentration.

Experimental

Short lengths of copper wire were cut into small pieces which were cleaned by warming 1:1 hydrochloric acid and water for 15 min followed by dipping into nitric acid and rinsing successively with tap water, distilled water, and ethanol.

Forty mg samples were taken for analysis. These were put on top of 5 mg of copper fluoride carrier in the sample electrode, and triplicates of each sample were burned according to the operating conditions described in Table 1. The spectrographic plates were developed according to standard procedures [4]. All intensities were corrected for background. A standard copper sample was included on each plate to correct any systematic error. Table 2 lists the analytical lines used.

Results and Discussion

The task was to find a pole with four wire remnants matching in trace concentrations with the respective four strands in the coil.

TABLE 1—*Spectrographic conditions.*

Spectrograph: Jarrell-Ash 3.4 m on Wadsworth mount
Order: 1st order
Analytical gap: 4 mm
Slit width: 30 μ
Excitation: d-c arc
Current: 13-14 amp. (19 A on short circuit)
Polarity: Sample electrode positive
Pre-arcing: None
Arcing time: 10 seconds
Plate: Kodak spectrographic plate S.A. No. 1
Electrodes: Sample electrode catalogue No. 1398 (Met-Bay Inc.);
Counter electrode SPK L3751 (National Carbon)

TABLE 2—Analytical lines.

Element	Analytical Line in Angstrom
Sb	I ^a 2598.1
Pb	2614.2
Fe	II ^b 2631.3
As	I ^a 2780.2
Mn	2798.3
Sn	I ^a 2840.0
Ni	I ^a 3054.3

^a I line classified as emitted by normal atom.

^b II line classified as emitted by singly ionized atom.

Preliminary screening of samples from different poles resulted in a focus on poles 15, 16, and 17. More detailed work resulted in the agreement between the coil and the remnants from pole 16 as shown in Table 3. Out of 48 average concentrations determined, 32 or 67 percent are reproducible to better than 10 percent.

The results of neutron activation analysis are included in Table 4 for comparison purposes. The matching of the wire ends on pole 16 and the wires in the coil based on trace concentrations of Se, Au, Sb and Ag is again clear. A comparison of the antimony data in Tables 3 and 4 shows that less than 1 ppm of antimony is detectable by neutron activation

TABLE 3—Trace concentrations by emissions spectrograph (ppm).

	Sb	Pb	Fe	As	Mn	Sn	Ni
Coil-Wire 1	...	3.6(11) ^a	25	...	0.22	0.47(17) ^a	3.9
Pole 16-Wire 1	...	3.6	24(11) ^a	...	0.20	0.45	4.9
Coil-Wire 2	...	4.7(15) ^a	18	...	0.35	4.5(18) ^a	4.4(14) ^a
Pole 16-Wire 2	...	4.5	19	...	0.35(11) ^a	4.4(11) ^a	4.4
Coil-Wire 3	9.4	5.5	11	14	0.24	2.1	13
Pole 16-Wire 3	8.4	4.8	8.9(12) ^a	13	0.20	2.0	11
Coil-Wire 4	3.8(13) ^a	5.6(14) ^a	6.1(16) ^a	6.7	0.15(13) ^a	9.4	12(17) ^a
Pole 16-Wire 4	3.6	5.8	6.7(16) ^a	5.5	0.15(13) ^a	8.3	11

^a Coefficients of variation in percent based on triplicates are specified in parenthesis whenever these exceed 10 percent.

TABLE 4—Trace concentrations by neutron activation analysis (ppm).

	Se	Au	Sb	Ag
Coil-Wire 1	5.2	0.34	0.69	8.1(13) ^a
Pole 16-Wire 1	4.7(11) ^a	0.32	0.77	8.4
Coil-Wire 2	6.6	0.67	0.61	9.6
Pole 16-Wire 2	6.4	0.67	0.55(13) ^a	9.3
Coil-Wire 3	1.3	0.18(14) ^a	8.6	44.3
Pole 16-Wire 3	1.1	0.16	8.5	43.8
Coil-Wire 4	2.1	0.037	3.7	9.6
Pole 16-Wire 4	2.0	0.036	3.7	8.1

^a Coefficients of variation in percent based on triplicates are specified in parenthesis whenever these exceeding 10 percent.

analysis but not by emission spectrograph. This shows that neutron activation analysis is more sensitive than emission spectrography. Our preliminary work also showed that neutron activation analysis is the more precise of the two for this application. The close agreement of the average concentration results from emission spectrography with those from neutron activation analysis shows that the slope of the working curve, n , for antimony is close to 1.

Notwithstanding some sacrifice of sensitivity, precision, and possibly accuracy, the spectrographic method provides seven elements for comparison and takes only one-quarter of the time required in neutron activation analysis.

Summary

A spectrographic method for quantitatively determining Sb, Pb, Fe, As, Mn, Sn, and Ni in parts per million levels in single-stranded copper wires has been described. Its application was exemplified by an actual theft case.

There is an indication that neutron activation analysis excels in sensitivity, precision, and possibly accuracy; but the spectrographic method provides more elements for comparison and takes one-quarter the time required by neutron activation analysis.

The spectrographic method gives apparent concentration values when the slope of the working curve for the trace element in question differs from 1. If the slope approaches 1, as in this work, the concentration values obtained are close to true values. In any case, apparent concentrations are adequate for the comparison of copper wires in forensic cases.

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Centre of Forensic Sciences
8 Jarvis Street
Toronto 2, Ontario
Canada