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Identification of Single-Stranded Copper Wires by Nondestructive Neutron Activation Analysis

The great demand and high price of copper has, in recent years, resulted in a large number of thefts from construction sites, warehouses, storage areas, and private homes. Copper wire has been stripped from telegraph and hydroelectric poles. Expensive multiple-conductor cables have been stolen and the insulation burned off in order to recover a relatively small amount of copper scrap. In most cases it has been a difficult task to identify the wire, since copper wires are usually drawn from high purity refined ore and few analytical procedures are sufficiently sensitive to quantitatively determine the amount of trace elements present. Neutron activation analysis has a high sensitivity for a large number of elements. Consequently, this method is chosen when other analytical procedures, such as atomic absorption spectrophotometry and emission spectrography, fail to give useful results.

Two smelting companies handle most of the copper concentrate refined in Canada and convert it into bars of 99.99 percent purity for processing into the final form. These companies extract much of their concentrate directly from the ore but they also buy concentrate from a number of other Canadian companies. Practically all the ore is mined in Canada; only a minor amount is imported. The variation in the amount of trace impurities in the refined bars has been reported[2] to be negligible both in shipments from the same refinery and from different refineries throughout the world.

The refined bars of 99.99 percent pure copper are sold to about five major rolling mills and wire manufacturers, where they are rolled into rods $\frac{5}{8}$ in. in diameter which are eventually drawn into wires of various diameters. Since the amounts of copper wire imported into Canada[3] are negligible, it would be expected that there would be little variation in the trace element concentrations of their wires. However, in the course of rolling the bars into rods and then drawing the rods into wires, additional trace element contamination can be introduced. These, together with the impurities originally present in the refined bars, account for the variations in the amount of trace elements present in copper wire.

Experimental

Short lengths of copper wire were cut into small specimens, which were cleaned by dipping into dilute nitric acid and rinsing successively with tap water, distilled water, and ethanol. Eight to 10 mg specimens were then taken for analysis. Five replicate determinations were made for each wire on specimens cut from a length not exceeding 1 cm. These

were packed together with standards and irradiated in a neutron flux of approximately 1.5×10^{13} n/cm²·s for 40 h in the nuclear reactor at McMaster University.

After about 12 days they were counted for 128 min using a high resolution 30 cm³ Ge-Li detector connected to a Kicksort 4096 multichannel pulse height analyzer. This waiting period allowed sufficient time for ^{64}Cu, with a half-life ($t_{1/2}$) of 12.8 h, to decay sufficiently to reveal the longer half-lived traces: ^{75}Se ($t_{1/2}$, 127 days), ^{198}Au ($t_{1/2}$, 2.7 days), ^{124}Sb ($t_{1/2}$, 60 days), and ^{110m}Ag ($t_{1/2}$, 270 days). Although ^{60}Co ($t_{1/2}$, 5.3 years) was also observed, its usefulness for Co trace determination was masked by the side reaction of the copper matrix, ^{63}Cu (n,α) ^{60}Co. The more sensitive ^{122}Sb ($t_{1/2}$, 2.8 days) was interfered with by ^{76}As ($t_{1/2}$, 26.6 h) and, therefore, ^{124}Sb was used.

Results and Discussion

The concentrations of the trace elements, together with the coefficient of variation based on five determinations, for the twelve single-stranded wires studied are compiled in Table 1.

TABLE 1—*Concentrations[a] of trace elements in single-stranded copper wires.*

Copper Wire Specimen	Source	Gage	Se		Au		Sb		Ag	
			C	V	C	V	C	V	C	V
1	Bell Telephone	8	9.2	8.2	0.60	3.4	0.44	17	25	11
2	Canada Wire	8	3.2	8.8	0.094	2.2	0.96	7.9	13	5.1
3	Canada Wire	9	3.3	11	0.065	3.2	0.37	26	14	7.4
4	Canada Wire	14	1.7	11	0.042	5.0	0.32	25	9.3	4.5
5	Canada Wire	19	4.3	4.3	0.070	2.9	0.47	9.4	13	5.8
6	Canada Wire	21	4.7	12	0.14	7.7	0.34	17	13	7.1
7	Canada Wire	3	4.9	5.8	0.16	13	0.40	16	15	4.4
8	Canada Wire	18	2.1	8.7	0.11	27	0.20	15	9.8	5.9
9	Canada Wire	18	1.7	5.6	0.087	11	0.14	26	11	6.2
10	Old telegraphic wire	5	7.1	2.6	0.25	8.3	8.1	3.8	18	2.9
11	Old telegraphic wire	8	7.6	14	0.31	6.7	12	8.1	27	4.0
12	Old telegraphic wire	8	8.9	8.4	0.49	8.5	5.4	6.8	26	5.9
Specimens 1 to 12 C max /C min			5		14		86		3	
Specimens 2 to 9 C max /C min			3		4		7		2	

[a] C = average concentration in ppm; V = coefficient of variation in %.

Selenium, gold, antimony, and silver concentrations varied substantially and irregularly among the twelve wires. In the case of wires from the same manufacturer (specimens 2 to 9) the trace variations were smaller but still sizeable. For example, the ratio of the maximum concentration to the minimum concentration of antimony for the nine wires from the same manufacturer was 7, as against 86 for the total of twelve wires. The irregular pattern of trace variations among the wires is not surprising, since the trace variations are the total of the impurities originally present in the refined wire bars and the contaminations added during the wire processing. Higher trace concentrations were found in the old specimens 10, 11, and 12 than in all others except specimen 1. This may be due to the inferior refining methods used for the older wires.

The cobalt trace concentrations were on the order of 1.8 to 2.1 ppm and were constant as previously explained. Caldwell[4] reported sizeable differences in cobalt concentration

4 Caldwell, R. J., "Comparison of PVC coated samples of copper cable by neutron activation analysis," *Journal of the Forensic Science Society,* FSSJA, Vol. 10, 1970, pp. 69–72.

among the wires and cables in his study. These, however, were wires of no better than 99.8 percent purity, judging from a maximum reported zinc concentration exceeding 2000 ppm. Wires in the present study were about 99.99 percent pure.

Out of 48 concentration averages for selenium, gold, antimony, and silver, 12 were reproducible to better than 5 percent and 33 to better than 10 percent. The maximum coefficient of variation was 27 percent. These degrees of precision are satisfactory for most case applications but could be improved, if necessary, by substantially increasing the counting time from the 128-min counting interval used in this work.

Typical Case Applications

Case 1

The first application involves a case of stolen telegraphic wires. Four lengths of copper wire (A_1, A_2, A_3, A_4) found at the scene of the theft were to be compared with a length of copper wire (B) seized at a scrap yard and suspected of being stolen. All were bare, single-stranded wires with the same general physical appearance and a diameter of 0.28 cm.

Triplicate specimens were taken along the lengths of all five wires and were subjected to neutron activation analysis. The trace concentrations are listed in Table 2. While the four control wires are distinguishable from each other, control A_1 and the suspected stolen wire B match well within experimental error. Using a t test[5] at a level of significance of 0.02, it can be shown that wire B is significantly different from all controls except A_1.

TABLE 2—Concentrations of trace elements—case 1 (ppm).

	Se	Au	Sb	Ag
Control wires				
A_1	2.4 ± 0.2	0.047 ± 0.003	0.16 ± 0.01	12.7 ± 0.07
A_2	3.5 ± 0.4	0.064 ± 0.013	0.27 ± 0.07	17.2 ± 1.0
A_3	2.6 ± 0.2	0.050 ± 0.006	0.20 ± 0.01	13.3 ± 1.3
A_4	1.9 ± 0.1	0.034 ± 0.002	0.21 ± 0.02	12.6 ± 0.03
Suspect wire				
B	2.3 ± 0.1	0.042 ± 0.008	0.15 ± 0.02	13.0 ± 0.05

Case 2

A theft of copper wire cable was reported from a paper mill. This cable, of $1\frac{1}{16}$ in. outside diameter, was comprised of 37 strands of $\frac{1}{8}$-in.-diameter tin-coated copper wire and was surrounded by an inner layer of Mylar film, a middle layer of rubber, and an outermost layer of fibrous material. Some red lettering was legible on the fibrous material. A 6-in. portion of control cable (A) obtained from the paper mill was to be compared with ten portions of copper cables (B) of various lengths found in the suspect's car. These had the same appearance as the control. Neutron activation analysis was applied to triplicate specimens of the middle strand A_1 and one other arbitrarily selected strand A_2 of the control and the middle strand of suspect cable B. Triplicate specimens of B were taken randomly from the ten portions available.

The results are summarized in Table 3. While A_1 and A_2 are clearly distinguishable, the middle strands A_1 and B match well within experimental error. It was concluded that the suspect cable and the control cable had a significant probability of common origin. In this connection it should be mentioned that Caldwell,[4] in his investigation of a 19-strand wire

[5] Freund, J. E., *Modern Elementary Statistics*, Prentice Hall, Englewood Cliffs, N.J., 1960, p. 270.

TABLE 3—*Concentrations of trace elements—case 2 (ppm).*

		Se	Au	Sb	Ag
Control cable	Middle strand A_1	1.44 ± 0.04	0.071 ± 0.002	0.11 ± 0.01	9.1 ± 0.4
	One arbitrary strand A_2	0.99 ± 0.04	0.047 ± 0.002	0.11 ± 0.01	7.9 ± 0.1
Suspect cable	Middle strand B	1.42 ± 0.07	0.069 ± 0.003	0.11 ± 0.01	9.0 ± 0.8

cable by neutron activation analysis, appeared to base his findings on the average trace concentrations of all 19 strands rather than on the results from individual strands. In this work, single strands, specifically the middle strands, were used for comparison.

Summary

A method for determining quantitatively selenium, gold, antimony, and silver in parts per million levels in single-stranded copper wires by nondestructive neutron activation analysis has been outlined. Its application to actual theft cases involving identification of copper wires and cables has been described .

Whether the copper wires are manufactured by the same or different manufacturers, the variations of trace concentrations among them have been attributed to the contamination resulting from processing, together with whatever trace variations were present in the refined bars prior to processing. These trace variations have been found to be random in nature.

In the case applications, the possibility of variations along the length of wires has been considered by sampling at different points along the length of wire. There was no indication of variations for the lengths and cases in question. This possibility should, of course, always be examined in actual applications.

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