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A NON-DESTRUCTIVE X-RAY FLUORESCENCE METHOD FOR ANALYSIS OF METAL ALLOY WIRE SAMPLES

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ABSTRACT

Although quantitative analysis of metal alloys is typically accomplished by wet-chemical techniques, complete dissolution of some metal alloys can be difficult. Here, we report an alternative non-destructive energy dispersive x-ray fluorescence (EDXRF) method for determination of nickel, gold, copper, and silver in metal alloy wires. Sample preparation is simple and consists of mounting wires as a single strand in machined polyethylene sample cups. Wires are analyzed in two symmetrical positions nearly parallel to the x-ray beam, thereby improving the external reproducibility of the analysis. Ideally, standards and samples are matched in terms of chemical composition and diameter. For 50 mil copper-silver wire, four certified reference wires consisting of various copper-silver compositions and matching the unknown diameter were used. However, we also investigated standards of different elemental composition and thickness. For analysis of 25 mil nickel-gold wires, 20 mil NIST standard wires consisting of copper-gold were applied for standardization and compared with certified 25 mil nickel-gold standards. Variations in wire diameter were corrected using an infinite thickness approximation, and nickel intensities were calculated from the copper intensities using a fundamental parameters calculation. The standard curves obtained from both approaches are similar, indicating that wires of varying thickness and composition can be applied as standards. Analysis of copper-silver and nickel-copper wire "unknowns" agrees with certified values to better than 0.3 wt %. We conclude that this rapid, non-destructive method could be a useful alternative to wet-chemical methods for many applications.

BACKGROUND

Quantitative analysis of metal alloy samples is typically accomplished by standard wet chemical methods, such as gravimetry or plasma spectrometry. However, these techniques are destructive requiring complete dissolution of the alloy, and some metal alloys can be difficult to dissolve with standard strong-acid digestion methods. In these cases and others, X-ray methods may provide a useful alternative for metal alloy analysis.

Sample preparation for x-ray analysis of metal samples depends on the geometry of the object to be analyzed (Bertin, 1975). For non-uniform shapes or sizes, samples can be melted and shaped to form a flat surface (Fahlbusch, 1963). The drawback of this method is that sample composition can be altered during the melting process. However, many geometric objects can be analyzed directly with little sample preparation. For wire or rod of small diameter, previously reported techniques for obtaining a geometrically reproducible specimen include mounting by the wax-impression mold technique (Zimmerman, 1961) and the rotating spindle technique (Bertin and Longobucco, 1962).

In this paper, we outline the development and evaluation of a rapid, non-destructive X-ray method for quantitative analysis of metal alloy wire samples for quality assurance purposes at Los Alamos National Laboratory. The quality assurance requirements for these metal alloys require that the measurements have an error of less than +/- 1 wt %. The specific alloys investigated included copper-silver (Cusil) and nickel-gold (Nioro), although this method should be applicable to wires of a range of size and composition.

METHOD

Instrumentation: All analyses were performed using a commercial EDXRF spectrometer, a Spectrace 5000. This instrument has an X-ray tube source with variable source current and voltage up to 1 mA and 50 kV, which permits optimization of excitation conditions for the element of interest. The beam size is ~ 7 mm in diameter. The instrument is also equipped with a high-resolution , electrically cooled Si(Li) detector which permits simultaneous collection of X-rays of variable energy with minimal spectral interference. The instrument has a fundamental parameters data reduction package which was used as an aid in some of the data reduction in this study (Criss and Birks, 1968).

Specimen Preparation/Mounting: Wire samples and standards are mounted as a single strand in machined polyethylene sample cups (Figure 1). No other sample preparation is required, hence the method is fast and non-destructive. This provides a useful alternative to wet chemical methods (e.g. gravimetry or plasma spectrometry) for metal alloys (e.g. Cusil) which are difficult to completely dissolve.

Analysis Parameters: The following analysis conditions were used for both standards and samples. For the 50 mil copper-silver alloys: Cu K: tube voltage =35 kV, tube current =0.50 mA, livetime = 200 s, filter = 0.13 mm Pd. Ag K: tube voltage = 50 kV, tube current = 0.50 mA, livetime = 200 s, filter = 0.63 mm Cu. For the 25 mil nickel-gold alloys: Ni K and Au L: tube voltage =35 kV, tube current =0.90 mA, livetime = 200 s, filter = 0.13 mm Pd.

Orientation: A grating ring was affixed to the sample turret as an aid in reproducing the geometry of the analysis (Figure 2a). As shown in Figure 2b, peak intensities are sensitive to orientation of the wire relative to the x-ray beam, with maximum intensity obtained in a position parallel to the beam (~270^{o}).

External Precision/Replication: Due to possible asymmetry in wire mounting, replication or external precision is best when the average of two symmetrical, nearly parallel orientations is used for each analysis. This provides a geometric average similar to the rotating spindle technique, but provides an advantage in maintaining the maximum intensity of the x-ray signal at the position nearly parallel to the beam. Using this approach, the relative standard error in copper K intensity for three aliquots of Cusil wire is reduced from 0.5% to 0.1%. Similarly, the relative standard error in gold L intensity for three aliquots of Nioro wire is reduced from 0.6% to 0.3%.

50 Mil Copper-Silver Standardization: Four certified reference wires of 50 mil thickness spanning the composition of the Cusil wire were obtained from a second manufacturer. The compositions of these standards are listed below:

Braze 503-VTG: Ag = 50.22%, Cu = 49.78%
Braze 721-VTG: Ag = 71.35%, Cu = 28.63%
Braze 750: Ag = 75.71%, Cu = 21.00%, Zn = 3.17%
Lithobraze 925: Ag = 92.46%, Cu = 7.32%, Li = 0.22%

For both copper and silver, the K peak intensities were fit to quadratic calibration curves (Figures 3a and 3b), and high correlation coefficients (R^2 = 0.998-1.000) were obtained. Linear calibration curves yielded poorer fits to the data. Standardization uncertainty is determined for Cusil wire by comparing the certified values for BR721 with those obtained from the measured intensity and intensity-concentration relationship. The difference between these two concentrations is one estimate of the standardization uncertainty. An error of 0.2 wt % is assumed for the certified values for the standards (Lucas-Milhaupt, personal communication). After error propagation, the total error due to standardization is estimated to be on the order of 0.3 wt % for copper and 0.6 wt % for silver at the composition of interest (~29% Cu, 71% Ag).

25 Mil Nickel-Gold Standardization: Three certified reference wires of 25 mil thickness spanning the composition of the Nioro wire were obtained from a second manufacturer. In addition, six certified reference wires of ~20 mil thickness and consisting of copper-gold mixtures were obtained from NIST (SRM 482). The compositions of these standards are listed below:

70AU/8PD/22NI VTG: Au = 69.69%, Ni = 22.39%, Pd = 7.92%
82AU/18NI: Au = 81.87%, Ni = 18.11%
50AU/25PD/25NI VTG: Au = 49.83%, Ni = 25.27%, Pd = 24.90%
AU100: Au = 100.00%
AU80-CU20: Au = 80.15%, Cu = 19.83%
AU60-CU40: Au = 60.36%, Cu = 39.64%
AU40-CU60: Au = 40.10%, Cu = 59.92%
AU20-CU80: Au = 20.12%, Cu = 79.85%
CU100: Cu = 100.00%

Variations in wire diameter (measured by a micrometer) were corrected using an infinite thickness approximation, since the X-ray penetration depth (~35 um; Jenkins et al., 1995) is short relative to the wire diameter (500 um). Nickel intensities were calculated from the copper intensities using a fundamental parameters calculation (e.g. Criss and Birks, 1968). For both nickel and gold, peak intensities were fit to quadratic calibration curves for all of the standards (Figures 4a and 4b), and high correlation coefficients (R^2 = 0.997) were obtained. Linear calibration curves yielded poorer fits to the data. Agreement between the standard curves from the manufacturer and NIST indicate that infinite thickness and fundamental parameters corrections can be applied to quantify wires of varying thickness and composition.

Standardization uncertainty is determined for Nioro wire by comparing the certified values for Alloy 82AU/18NI with those obtained from the measured intensity and intensity-concentration relationship. An error of 0.2 wt % (2σ) is assumed for the certified values for the secondary manufacturer standards and 0.1 wt % for the NIST standards. After propagation of these errors, the total error due to standardization is estimated to be on the order of 0.4 wt % for nickel and 1.2 wt % for gold for the composition of interest (~18% Ni, 82% Au).

Method Results and Accuracy: Relative uncertainties and accuracies for the method are presented in Table 1. Utilizing the method discussed above, three aliquots of the Cusil wire yield the following average results: Cu = 28.4 +/- 0.4 %; Ag = 71.4 +/- 0.6 %. These agree with the manufacturer's certificate values for this material determined by wet chemical methods, which are Cu = 28.5 % and Ag = 71.5 %. Similarly, three aliquots of the Nioro wire yield the following average results: Ni = 18.1 +/- 0.4 %; Au = 81.7 +/- 1.3 %. These also agree with the manufacturer's certified values for this material (Ni = 18.3 % and Au = 81.7 %).

DISCUSSION

The method developed and evaluated here for quantitative analysis of metal alloy wire samples by EDXRF methods has both advantages and disadvantages relative to standard wet-chemical methods. The main advantages are that it is a rapid, non-destructive method with little sample preparation or waste generation. In addition, impurity identification and semi-quantitation are easily obtained from examination of the x-ray spectra. The external precision of the analysis is relatively high (0.1 – 0.3% $1\sigma_m$) and suitable for quality assurance purposes at Los Alamos National Laboratory, and it approaches the precision of gravimetric methods (< 0.2 wt %). The main limitation relative to gravimetric methods appears to be the requirement of construction of a standardization curve for each element and the introduction of standardization errors on the order of 1 to 2% relative.

There are practical limitations of this method in terms of the applicable size range of wires and the availability of standards. For example, wires considerably thinner than the 20-50 mil range in this study might produce lower peak intensities and have geometries which are more difficult to replicate, producing results with greater analytical uncertainties. In comparing the 25 mil Nioro and 50 mil Cusil wires, we do find that the thinner wire has greater relative analytical uncertainty. Another potential problem is that in some cases, wire standards of appropriate diameter and composition may not be easily available. However, we have shown that it is possible to apply infinite thickness and fundamental parameter corrections to a variety of standards, allowing wires of varying thickness and composition to be used as standards for the analysis.

ACKNOWLEDGMENTS

We thank G. Havrilla, G. Brooks, G. Roybal, L. Hunt, and L. Davenhall for helpful discussions. This project was conducted for the Materials Testing Laboratory (MTL) at Los Alamos National Laboratory (LANL). Support for the MTL comes from the Pit Manufacturing Project Office at LANL.

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TABLES

Table 1. EDXRF Method Precision and Accuracy

Element	Standardization Uncertainty (%)	External Precision (% $2\sigma_m$)	Total Propagated Uncertainty (% $2\sigma_m$)	Average Accuracy (%)
Copper	1.0	0.2	1.2	99.7
Silver	0.8	0.2	0.8	99.9
Nickel	2.2	0.6	2.2	98.9
Gold	1.5	0.6	1.6	100.0

FIGURE CAPTIONS

Figure 1. Photo of 50 mil Cusil and 25 mil Nioro wires mounted in sample cups.

Figure 2a. Photo of grating ring to provide reproducible geometry for the analysis.

Figure 2b. Orientation dependence of Cu K alpha line intensity for Cusil wire. Highest intensity is obtained for an orientation nearly parallel to the x-ray beam.

Figure 3a. Standardization curve for copper in 50 mil copper-silver alloy wire.

Figure 3b. Standardization curve for silver in 50 mil copper-silver alloy wire.

Figure 4a. Standardization curve for gold in 25 mil nickel-gold alloy wire. Intensities for the 20 mil NIST standards are corrected to 25 mil using an infinite thickness approximation.

Figure 4b. Standardization curve for nickel in 25 mil nickel-gold alloy wire. Intensities for the 20 mil NIST standards are corrected to 25 mil using an infinite thickness approximation, and copper intensities are converted to nickel intensities through use of a fundamental parameters calculation.

Figure 1.

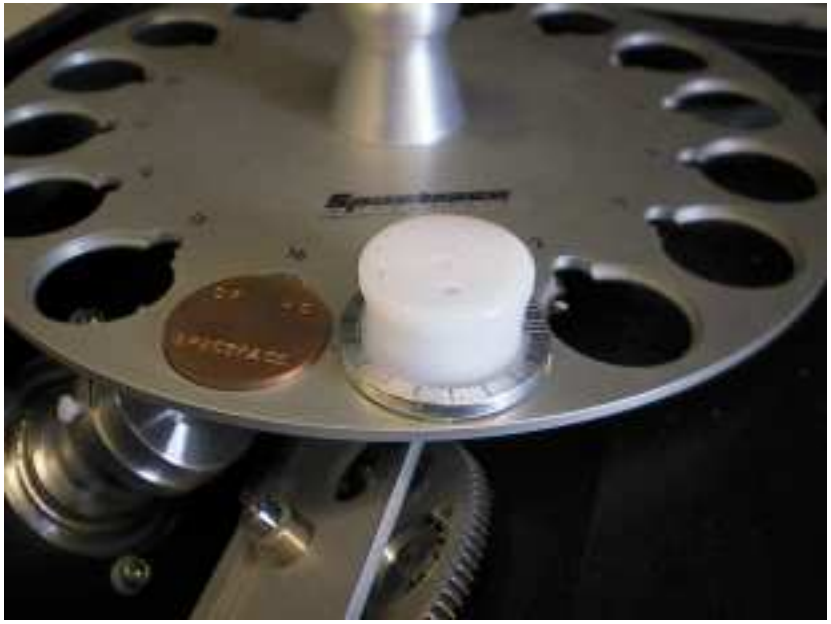
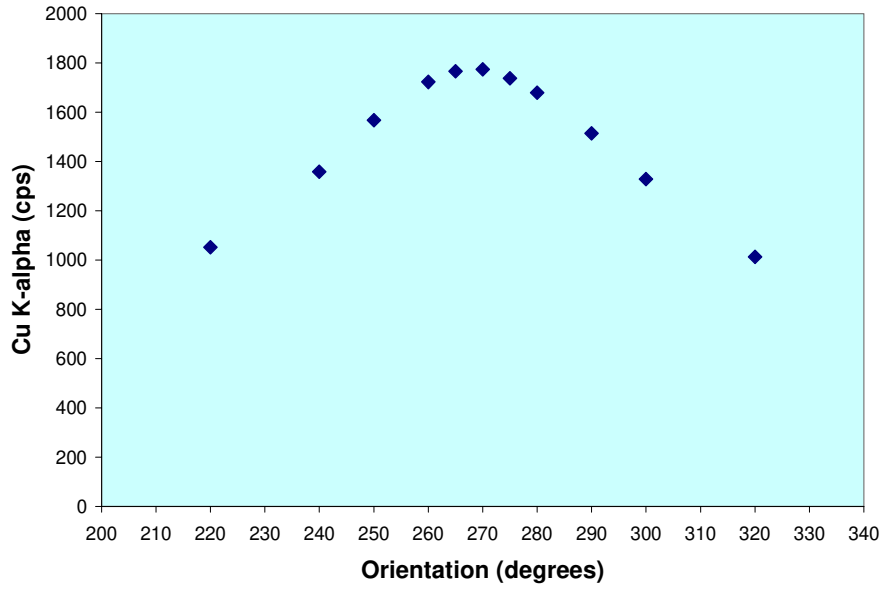


Figure 2a.

Figure 2b.



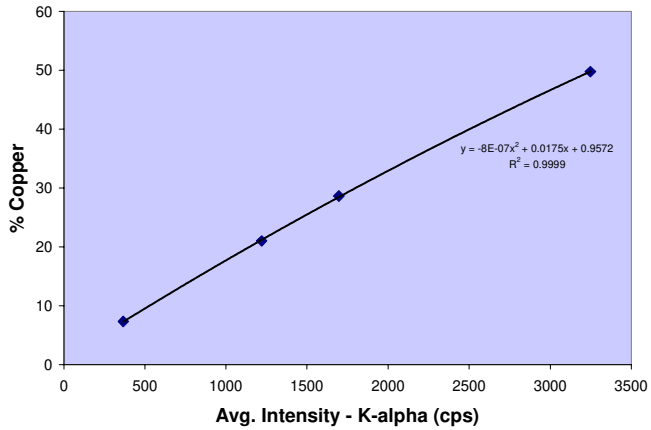


Figure 3a.

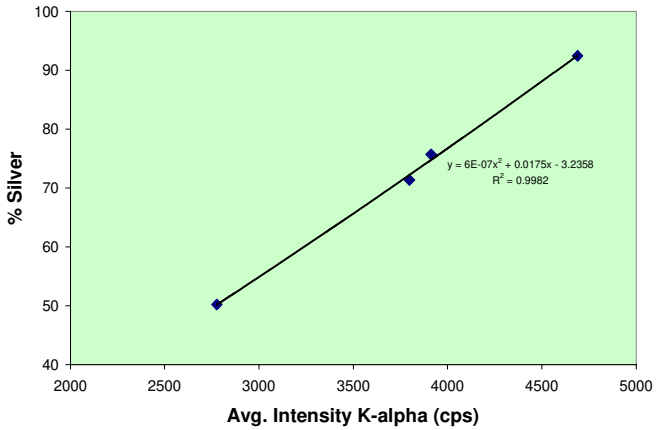


Figure 3b.

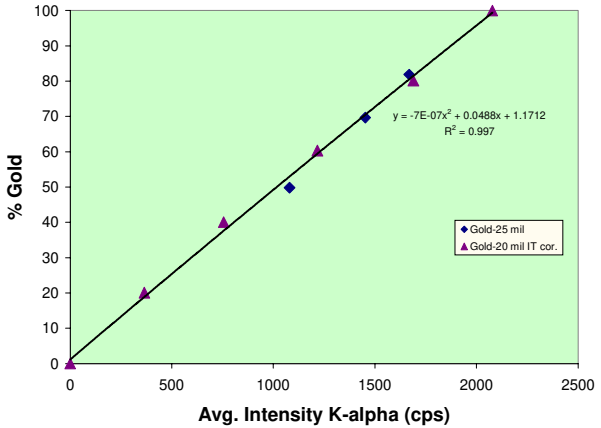


Figure 4a.

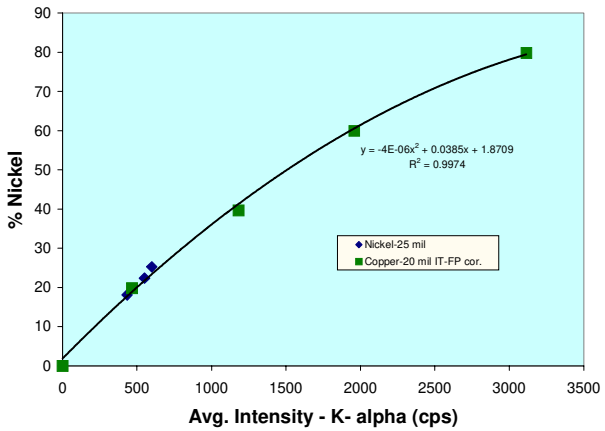


Figure 4b.