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DETERMINING TRACE METALS
IN GOLD DEPOSITS AND
PLATING BATHS

Technological Spinoff Report

L. L. Lantz, Project Leader

March 1973

Prepared for the
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**Kansas City
Division**

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Project Leader:
L. L. Lantz
Department 814

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DETERMINING TRACE METALS IN GOLD DEPOSITS AND PLATING BATHS

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Prepared by L. L. Lantz, D/814

Procedures are given for determining trace metals in gold plating solutions and gold deposits using atomic absorption spectrophotometry.

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SUMMARY

A procedure for determining 1- to 100- μ g quantities of metal impurities in gold plating solutions and gold plates has been established. The procedure was needed for a high-purity gold plating project and for analyzing gold-plated electrical contacts on electromechanical components. The Method of Additions was used to determine trace metals in gold plating solutions. Procedures for sample preparation and analysis of trace metals in gold deposits were evaluated.

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DISCUSSION

SCOPE AND PURPOSE

A procedure was needed for the determination of 1- to 100 μg quantities of trace metals in gold plates and gold plating solutions. Selection of a gold plating bath to plate high-purity deposits (99.9 percent Au minimum) under production conditions requires determining iron, copper, nickel, chromium, cobalt, and cadmium in trace quantities in the plating solutions and the plate. Troubleshooting electromechanical components like the SA1905 requires determining the purity of gold plate on miniature electrical contacts.

Specifications allow no single impurity greater than 0.1 percent. In addition the combined percentage of iron, nickel, and cobalt shall not be greater than 0.05 percent; and iron, nickel, and cobalt individually not greater than 0.03 percent. Other trace metals of interest are copper, chromium, cadmium, silver, tin, lead, and zinc.

The atomic absorption spectrophotometer (AAS) is best suited for these analyses because of its speed, ease of operation, relatively low cost, and its precision and accuracy. This project was established to develop suitable AAS procedures.

ACTIVITY

Determining trace metal quantities less than 100 μg in gold plating solutions and gold deposits by atomic absorption spectrophotometry involved dissolving the sample (if necessary), eliminating or compensating for interferences, diluting the sample, and obtaining meaningful quantitative data.

A Perkin-Elmer Model 403, Atomic Absorption Spectrophotometer (AAS) was used. Three readout modes are available on this instrument: digital voltmeter with an average readout of ten data points (DVM-10 AVE), 100 data points (DVM-100 AVE), and a RECORDER readout. The DVM-10 AVE takes about 1 second per reading, and the DVM-100 AVE about 10 seconds. The burner has a sample aspiration rate of 6 cm^3/min . The instrument settings used were in accordance with the Perkin-Elmer methods manual.

Trace Metals in Gold Plating Baths

An analytical procedure was sought which would be applicable to a variety of gold plating solutions. No sample preparation was required since the trace metals were already in solution; however, approaches to eliminating interferences were reviewed. Examination of all potential interferences was

impossible because of the time limitations, and because the complete composition of some proprietary baths were not known. Therefore, the Method of Additions was selected as best suited for analysis of trace elements in gold plating solutions. The Method of Additions is a standard analytical procedure which can be used when the effects of sample matrix components are difficult to eliminate. The results are accurate to within about 3 percent when the solids content of the sample is below 2 percent.

Trace Elements in Gold Plates

Methods were needed to separate the gold plate from its substrate. The most feasible methods were to peel the gold away from the substrate, dissolve the substrate away from the gold, and partially dissolve the gold away from the substrate. The last method was not tried since it is possible to contaminate the sample by dissolving substrate material through pinholes in the gold plate.

Gold from the plating solutions was plated on a passivated stainless steel rod and then peeled from the rod for analysis. Gold plates on portions of electro-mechanical components were separated by dissolving the substrates. The dissolution rates of iron, copper, and nickel plated with gold were observed in concentrated and six-molar nitric and hydrochloric acids. Copper and nickel substrates dissolved faster in six-molar nitric acid. Iron substrates dissolved faster in hot, concentrated hydrochloric acid. The gold samples were rinsed, dried, weighed, and dissolved in aqua regia (HCl:HNO₃--3:1). Ultrex (J. T. Baker Chemical Company) purity nitric and hydrochloric acids were used to prevent contamination of the sample.

According to Slavin*, mutual interferences by the trace elements present in the sample are limited to nickel and chromium. If iron and chromium are present, a lean air-acetylene flame must be used for nickel. A nitrous oxide-acetylene flame must be used for chromium if iron and nickel are present. The sample solutions will generally contain gold in sufficient quantities to cause matrix interferences, resulting in an enhancement of the absorption signal. Experiments indicated that aqua regia also enhanced the absorption signal. Therefore, gold and aqua regia were added to the standard solutions to compensate for the interferences.

The next step was to determine the appropriate volume to which the sample solution was to be diluted for analysis. This dilution volume depended on the quantity and number of trace elements present.

*Walter Slavin, "Atomic Absorption Spectroscopy," Interscience Publishers, New York, New York, 1968.

The gold samples were divided into two groups: those which could be analyzed by conventional AAS techniques and those which could not. The detection limits of the AAS using conventional techniques set the minimum quantity of metal which could be determined and the maximum volume to which the solution could be diluted for conventional analysis. A solution of an element cannot be diluted beyond its minimum detectable concentration. The rate at which the AAS aspirates a sample into the flame atomizer places a limit on the amount of solution available for the analysis of each element, if several are to be determined.

When the composition ranges and the elements to be determined were preset, the maximum dilution volume was estimated by dividing the approximate trace metal weight in μg by the largest detection limit involved. The maximum dilution volume was divided by the number of elements to be determined to obtain the solution volume available for the analysis of each element. The data readout technique was sometimes dictated by the volume available (Table 1). These volumes are required by the Perkin-Elmer 403 AAS, which has an aspiration rate of $6 \text{ cm}^3/\text{min}$ ($0.1 \text{ cm}^3/\text{s}$).

Table 1. Minimum Volume per Element Required for Each Readout Method

Element	Volume
DVM 100 AVE	1.5 cm^3
DVM 10 AVE	0.5 cm^3
RECORDER	0.2 cm^3

When the trace element composition was not known, an experimental approach was taken. The sample was diluted to 2 cm^3 , then divided into two equal parts. One part was retained for the final analysis. The second part was diluted to 5 cm^3 . The RECORDER readout mode was used to make qualitative determinations of the expected trace elements and to estimate the quantities involved. Based on these results, the remaining sample was diluted to the appropriate volume and used for quantitative measurements.

If the quantities and numbers of trace metals were such that less than 0.2 cm^3 was available for each elemental analysis, microsampling techniques were required.

Conventional Atomic Absorption Analysis

The sample concentrations were read from the DVM when there was sufficient sample to allow enough time for visual observation, because the method is faster. Experience showed that use of the DVM-10 AVE mode was satisfactory if the readings were not fluctuating. When there was considerable fluctuation in the readings, the DVM-100 AVE gave a better statistical average. When there was insufficient sample to use the DVM, the RECORDER readout was used.

Scale expansion was used to improve the readability of small absorption signals from solution concentrations less than $0.5 \mu\text{g}/\text{cm}^3$. However, scale expansion was accompanied by considerable signal fluctuation and zero (baseline) drift. When a recorder was used, the zero drift was included in the data. A straight line was drawn through the recorder baseline, permitting the baseline at each sample reading to be determined and subtracted from the sample. However, this introduced operator error into the results.

A method was worked out for using the digital voltmeter with the scale expansion technique. The following settings were made on the Perkin-Elmer 403: CONCENTRATION Button-IN, 100 AVERAGE--IN, and CONCENTRATION DIAL-10.00.

Readings for standard iron solutions and water were made in the following sequence: water, $0.2 \mu\text{g}/\text{cm}^3$ Fe, water, $0.1 \mu\text{g}/\text{cm}^3$ Fe, water, $0.05 \mu\text{g}/\text{cm}^3$ Fe, water, and $0.01 \mu\text{g}/\text{cm}^3$ Fe. Three 100 AVE readings were made for each sample and each water check. The sequence of measurements was performed three times. Results of the first sequence are given in Table 2. The numbers have arbitrary units and are of interest in relative terms. The zero drift can be seen in the water sample measurements.

The water sample readings were subtracted from the subsequent iron sample reading. The results of the three series of measurements are given in Table 3. Below $0.1 \mu\text{g}/\text{cm}^3$ Fe the accuracy falls off considerably, but it is possible to determine the order of magnitude down to about $0.01 \mu\text{g}/\text{cm}^3$. The average time required to change samples and take three 100 AVE readings was 51 seconds. At an aspiration rate of $6 \text{ cm}^3/\text{min}$, a 51-second aspiration required 5 cm^3 of sample solution. If ten elements are to be determined, a total of 50 cm^3 are required.

After the data in Table 2 had been examined, an additional water sample was included at the end of the sequence. The mean of the preceding and following water samples was then subtracted from each of the iron samples.

All of these measuring techniques required comparison of the sample to a standard. In the previous method the appropriate sequence was as follows: water, standard, water, sample and so on. The entire series can require several samples and standards. The highest precision analysis was made by a two-step method. In step one an approximate value of the sample was determined with a single standard. In the second step, two standard solutions were prepared which bracketed the sample within 5 percent on the high and low sides. The measurements were made and the results obtained by interpolation.

The data in Table 3 reveal that concentrations of $0.1 \mu\text{g}/\text{cm}^3$ or less cannot be determined accurately using conventional analysis. Microsampling techniques are required.

Analysis by Microsampling

If the sample available for each element is less than 0.2 cm^3 , or if the solution concentration is $0.1 \mu\text{g}/\text{cm}^3$ or less, a microsampling technique must be used. A relatively new flameless atomizer (or graphite tube furnace) was developed by Perkin-Elmer for this purpose. However, no flameless atomizer was available so a microsampling approach was tried with the flame atomizer. Accurately measured sample volumes of 0.1 cm^3 or less were placed on a spot test plate and aspirated into the flame. The capillary tube was placed quickly into the sample drop. The small sample droplet passes through the flame very rapidly and the absorbance of the sample produces a sharp peak on the recorder. The peak height is a function of the metal concentration in the sample. Inconsistent technique in placing the capillary tube caused random errors. The reproducibility of the peak height depends on the volume and concentration of the sample droplet. Table 4 shows the results of a series of analyses of 0.01 cm^3 , 0.025 cm^3 , and 0.1 cm^3 samples of 1, 5, and $10 \mu\text{g}/\text{cm}^3$ iron solutions. Each volume-concentration combination was analyzed ten times. The peak heights were measured and the average and standard deviation calculated. Table 4 gives the standard deviation of the peak heights as a percentage of the average peak height.

The same measurements made on copper, cobalt, and nickel solutions gave similar results. The precision is good for 0.1 cm^3 samples in all cases. For solution concentrations under $1 \mu\text{g}/\text{cm}^3$ the precision is probably not improved over the conventional techniques.

In a typical analysis, a sample volume of 0.025 cm^3 was measured by a micropipet and placed on a spot test plate. The sample was aspirated into the flame and the peak recorded. The sample was compared with the same volume of a standard solution and the sample concentration estimated. Two standards were then prepared which bracketed the sample within 5 to 10 percent on each side. The sample and standards were then measured using

Table 2. Analysis of Iron Samples Using
Digital Readout With Scale Expansion

Analysis Number	Material	Average of Three Readings
1	Water	371
2	$0.2 \mu\text{g}/\text{cm}^3 \text{ Fe}$	521
3	Water	390
4	$0.1 \mu\text{g}/\text{cm}^3 \text{ Fe}$	458
5	Water	394
6	$0.05 \mu\text{g}/\text{cm}^3 \text{ Fe}$	439
7	Water	406
8	$0.01 \mu\text{g}/\text{cm}^3 \text{ Fe}$	422

Table 3: Average Values of Three Series of
Measurements Using Digital Readout
With Scale Expansion

Material	Average	Percent Deviation
$0.2 \mu\text{g}/\text{cm}^3 \text{ Fe}$	154 ± 8	5.2
$0.1 \mu\text{g}/\text{cm}^3 \text{ Fe}$	79 ± 7	8.9
$0.05 \mu\text{g}/\text{cm}^3 \text{ Fe}$	33 ± 8	24.2
$0.01 \mu\text{g}/\text{cm}^3 \text{ Fe}$	5 ± 7	100

Table 4. Microsampling With a Flame Atomizer
(Standard Deviation of Peak Heights as a
Percentage of the Average Peak Height)

Volume	Concentration		
	1 $\mu\text{g}/\text{cm}^3$	5 $\mu\text{g}/\text{cm}^3$	10 $\mu\text{g}/\text{cm}^3$
0.01 cm^3	20	8.3	5.5
0.025 cm^3	10	3.4	2.6
0.1 cm^3	2.1	2.1	1.5

0.1 cm^3 drops. The sample concentration was determined by interpolation.

Microsampling with a flame atomizer does not produce lower detection limits, or improve the precision of small sample measurements, but in the absence of a flameless atomizer it does provide the potential of analyzing one to two milliliter samples containing up to ten metals within the concentration detection limits of the instrument. It was not possible to accurately analyze samples under 0.1 $\mu\text{g}/\text{cm}^3$ without a flameless analyzer.

ACCOMPLISHMENTS

Procedures were set up for determining 1 microgram to 100 microgram quantities of trace metals in gold plating baths and gold deposits.

FUTURE WORK

A flameless atomizer is being procured and will be used to extend the analytical capability to lower concentrations and smaller volumes.