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# DETERMINATION OF COPPER, CADMIUM, AND IRON IN METAL CYANIDE WASTE SOLUTIONS BY ATOMIC ABSORPTION SPECTROSCOPY

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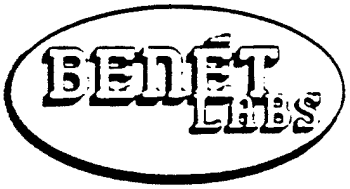


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# DETERMINATION OF COPPER, CADMIUM, AND IRON IN METAL CYANIDE WASTE SOLUTIONS BY ATOMIC ABSORPTION SPECTROMETRY

Sam Sopok

## ABSTRACT

The chemical literature lacks a specific analytical method to determine copper, cadmium, and iron in metal cyanide waste solutions which is needed to optimize the treatment and disposal of these metals. A specific method is presented in this report that provides acceptable analysis of these metals in this treatment process. The concentrations of these metals range from 0 to 500 ppm for these solutions, and the resulting precisions are in the range of 0.5 to 35 ppm. These results are supported by six years of testing.

## KEYWORDS

Chemical Analysis

Copper

Cadmium

Iron

Metal Cyanide

Waste Solutions

Atomic Absorption Spectrometry

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### TABLES

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## INTRODUCTION

The chemical literature lacks a specific analytical method to determine copper, cadmium, and iron in metal cyanide waste solutions which is needed to optimize the treatment and disposal of these metals. Lack of optimization of treatment and disposal of these waste solutions causes serious problems for the waste treatment industry such as failure to meet government disposal requirements and wasted resources.

A common chemical analysis method uses a method composed of an alkaline precipitation (refs 1,2). This method provides adequate precisions but an unacceptable analysis time of two days.

The specific method given in this report provides acceptable analysis and control of the metals in the waste solutions. The method consists of atomic absorption (AA) spectrometry (ref 3).

## EXPERIMENTAL PROCEDURE

Strict analytical chemistry methods and procedures are followed throughout this experimental section. An excellent source of reference for these methods and procedures is by Fritz and Schenk (ref 1).

Three analytical reagent grade standard solutions are required. They are 1.000 $\pm$ 0.005-g/l copper solution, 1.000 $\pm$ 0.005-g/l cadmium solution, and 1.000 $\pm$ 0.005-g/l iron solution. Each solution contains 50-ml of concentrated nitric acid per liter that meets American Chemical Society (ACS) and American Society for Testing and Materials (ASTM) Standards (ref 4).

One other reagent grade solution is required. It is concentrated nitric acid.

Three copper standards are prepared in 500-ml volumetric flasks for AA analysis. The copper concentrations of these are 5.00, 2.50, and 0.00 parts per million (ppm); these standard solutions contain nitric acid for stability.

Three cadmium standards are prepared in 500-ml volumetric flasks for AA analysis. The cadmium concentrations of these are 2.00, 1.00, and 0.00 ppm; these standard solutions contain nitric acid for stability.

Three iron standards are prepared in 500-ml volumetric flasks for AA analysis. The iron concentrations of these are 5.00, 2.50, and 0.00 ppm; these standard solutions contain nitric acid for stability.

All metal cyanide waste solution samples are prepared in triplicate in 500-ml volumetric flasks for their metal analyses by this method. A 1:100 dilution is required of these sample solutions; the samples also contain nitric acid for stability.

The analytical system used is the Perkin-Elmer* AA spectrometer. Reference 4 is an excellent source of reference for the operation and maintenance of this instrument.

The copper analysis operating conditions for the spectrometer are a 324.8-nm wavelength, 0.7-nm slit size, oxidizing air-acetylene flame, 25-mA lamp setting, and 2-second integration time.

The cadmium analysis operating conditions for the spectrometer are a 228.8-nm wavelength, 0.7-nm slit size, oxidizing air-acetylene flame, 8-mA lamp setting, and 2-second integration time.

*Perkin-Elmer Corporation, Norwalk, CT.

The iron analysis operating conditions for the spectrometer are a 248.3-nm wavelength, 0.2-nm slit size, oxidizing air-acetylene flame, 30-mA lamp setting, and 2-second integration time.

The standard and sample solution absorbance data are recorded using the procedures in Reference 4. Since the standard solution concentrations are known, sample solution concentrations can be calculated.

## RESULTS AND DISCUSSION

The calibration data are given for the standard copper, cadmium, and iron solutions in Tables I through III. The AA spectrometer is linear to 5-ppm copper and sensitive to 0.1-ppm copper, as shown in Table I; linear to 2-ppm cadmium and sensitive to 0.03 ppm cadmium, as shown in Table II; and linear to 5-ppm iron and sensitive to 0.1-ppm iron, as shown in Table III. If these data are found to be non-linear, then they must be acquired again.

Tables IV through VI present data for metal cyanide waste sample solutions of copper, cadmium, and iron, respectively. These sample solutions are diluted 1:100 in order to attain detector linearity. Due to a linear operating range, the following three simplified calculations are used to determine metal concentations in the original metal cyanide waste sample solutions:

$$\text{ppm Copper} = (500)(\text{sample absorbance}/5\text{-ppm standard absorbance}) \quad (1)$$

$$\text{ppm Cadmium} = (200)(\text{sample absorbance}/2\text{-ppm standard absorbance}) \quad (2)$$

$$\text{ppm Iron} = (500)(\text{sample absorbance}/5\text{-ppm standard absorbance}) \quad (3)$$

The sample solution in Table IV has a 422-ppm copper concentration according to Eq. (1); the sample solution in Table V has a 41-ppm cadmium concentration according to Eq. (2); and the sample solution in Table VI has a 289-ppm iron concentration according to Eq. (3).

It is useful to evaluate the variations in precision for the materials and methods used. Tables VII through XV present these data for the 2.500-ml micropipet, 1.250-ml micropipet, 1.000-ml micropipet, 0.500-ml micropipet, 5-ml pipet, the 500-ml class A volumetric flasks, 1.000-g/l copper standard solution, 1.000-g/l cadmium standard solution, and the 1.000-g/l iron standard solution, respectively. Variations in precision are also evaluated for the AA spectrometer. Table XVI presents these data for six consecutive replicates of the 5.00-ppm copper standard solution. Table XVII presents these data for six consecutive replicates of the 2.00-ppm cadmium standard solution. Table XVIII presents these data for six consecutive replicates of the 5.00 ppm iron standard solution.

The data by this specific method are sufficient to adequately optimize the treatment and disposal of these metals in the Watervliet Arsenal's metal cyanide waste facility according to its standard operating procedures (ref 5), thus providing efficient use of resources. The concentrations of these metals range from 0 to 500-ppm for these solutions, and the resulting precisions are in the range of 0.5 to 35-ppm. These results are supported by six years of testing.

## REFERENCES


1. J. Fritz and G. Schenk, Quantitative Analytical Chemistry, Allyn and Bacon, Inc., Boston, MA, 1987.
2. D. Peters, J. Hayes, and G. Hieftje, Chemical Separations and Measurements: Theory and Practice of Analytical Chemistry, W. B. Saunders Company, Philadelphia, PA, 1974.
3. H. Bauer, G. Christian, and J. O'Reilly, Instrumental Analysis, Allyn and Bacon, Inc., Boston, MA, 1978.
4. "AA/ICP Operators Manual," Perkin-Elmer, Inc., Norwalk, CT, 1976.
5. "Metal Cyanide Waste Solution Procedure," Dept. of Army, Watervliet Arsenal, Watervliet, NY, 1980.

TABLE I. STANDARD SOLUTION DATA FOR COPPER

| Replicate | Absor. (AU) 0.00 ppm Copper | Absor. (AU) 2.50 ppm Copper | Absor. (AU) 5.00 ppm Copper |
|---|---|---|---|
| 1 | 0.000 | 0.129 | 0.256 |
| 2 | 0.000 | 0.127 | 0.254 |
| 3 | 0.000 | 0.127 | 0.258 |
| X(avg) | 0.000 | 0.128 | 0.256 |

TABLE II. STANDARD SOLUTION DATA FOR CADMIUM

| Replicate | Absor. (AU) 0.00 ppm Cadmium | Absor. (AU) 1.00 ppm Cadmium | Absor. (AU) 2.00 ppm Cadmium |
|---|---|---|---|
| 1 | 0.000 | 0.086 | 0.178 |
| 2 | 0.000 | 0.089 | 0.174 |
| 3 | 0.000 | 0.089 | 0.176 |
| X(avg) | 0.000 | 0.088 | 0.176 |

TABLE III. STANDARD SOLUTION DATA FOR IRON

| Replicate | Absor. (AU) 0.00 ppm Iron | Absor. (AU) 2.50 ppm Iron | Absor. (AU) 5.00 ppm Iron |
|---|---|---|---|
| 1 | 0.001 | 0.100 | 0.199 |
| 2 | 0.000 | 0.103 | 0.195 |
| 3 | 0.000 | 0.098 | 0.197 |
| X(avg) | 0.000 | 0.100 | 0.197 |

TABLE IV. EXPERIMENTAL SAMPLE SOLUTION DATA FOR COPPER IN METAL CYANIDE WASTE SOLUTIONS

| Replicate | Sample Copper Absor. (AU) | Sample Copper Conc. (ppm) |
|---|---|---|
| 1 | 0.214 | 4.18 |
| 2 | 0.218 | 4.26 |
| 3 | 0.216 | 4.22 |
| X(avg) | 0.216 | 4.22 |

TABLE V. EXPERIMENTAL SAMPLE SOLUTION DATA FOR CADMIUM IN METAL CYANIDE WASTE SOLUTIONS

| Replicate | Sample Cadmium Absor. (AU) | Sample Cadmium Conc. (ppm) |
|---|---|---|
| 1 | 0.037 | 0.42 |
| 2 | 0.034 | 0.39 |
| 3 | 0.038 | 0.43 |
| X(avg) | 0.036 | 0.41 |

TABLE VI. EXPERIMENTAL SAMPLE SOLUTION DATA FOR IRON IN METAL CYANIDE WASTE SOLUTIONS

| Replicate | Sample Iron Absor. (AU) | Sample Iron Conc. (ppm) |
|---|---|---|
| 1 | 0.115 | 2.92 |
| 2 | 0.110 | 2.79 |
| 3 | 0.117 | 2.97 |
| X(avg) | 0.114 | 2.89 |

TABLE VII. PRECISION OF MICROPIPETTING 2.500 ml

| Replicate | Volume (ml)* |
|---|---|
| 1 | 2.531 |
| 2 | 2.505 |
| 3 | 2.484 |
| 4 | 2.501 |
| 5 | 2.525 |
| 6 | 2.477 |
| X(avg) | 2.504 |
| Sn | 0.021 |

*Volumes are calculated from the weight-volume relationship of each micropipetted deionized water solution corrected for temperature.

TABLE VIII. PRECISION OF MICROPIPETTING 1.250 ml

| Replicate | Volume (ml)* |
|---|---|
| 1 | 1.249 |
| 2 | 1.239 |
| 3 | 1.263 |
| 4 | 1.246 |
| 5 | 1.256 |
| 6 | 1.252 |
| X(avg) | 1.251 |
| Sn | 0.008 |

*Volumes are calculated from the weight-volume relationship of each micropipetted deionized water solution corrected for temperature.

TABLE IX. PRECISION OF MICROPIPETTING 1.000 ml

| Replicate | Volume (ml)* |
|---|---|
| 1 | 1.0133 |
| 2 | 1.0105 |
| 3 | 1.0140 |
| 4 | 1.0066 |
| 5 | 1.0106 |
| 6 | 1.0065 |
| X(avg) | 1.0102 |
| Sn | 0.0029 |

*Volumes are calculated from the weight-volume relationship of each micropipetted deionized water solution corrected for temperature.

TABLE X. PRECISION OF MICROPIPETTING 0.500 ml

| Replicate | Volume (ml)* |
|---|---|
| 1 | 0.4987 |
| 2 | 0.4998 |
| 3 | 0.5012 |
| 4 | 0.4999 |
| 5 | 0.5014 |
| 6 | 0.5003 |
| X(avg) | 0.5002 |
| Sn | 0.0010 |

*Volumes are calculated from the weight-volume relationship of each micropipetted deionized water solution corrected for temperature.

TABLE XI. PRECISION OF A 5-ml CLASS-A PIPET

| Replicate | Volume (ml)* |
|---|---|
| 1 | 5.01 |
| 2 | 5.00 |
| 3 | 5.01 |
| 4 | 4.99 |
| 5 | 4.99 |
| 6 | 4.99 |
| X(avg) | 5.00 |
| Sn | 0.01 |

*Volumes are calculated from the weight-volume relationship of a pipetted deionized water solution corrected for temperature.

TABLE XII. PRECISION OF 500-ml CLASS-A VOLUMETRIC FLASK

| Replicate | Volume (ml)* |
|---|---|
| 1 | 500.6 |
| 2 | 500.1 |
| 3 | 499.8 |
| 4 | 500.0 |
| 5 | 500.5 |
| 6 | 499.3 |
| X(avg) | 500.1 |
| Sn | 0.4 |

*Volumes are calculated from the weight-volume relationship of the contained deionized water solution corrected for temperature.

TABLE XIII. PRECISION OF 1.000-g/l COPPER STANDARD SOLUTION

| Replicate | Copper Conc. (g/l)* |
|---|---|
| 1 | 1.001 |
| 2 | 0.994 |
| 3 | 0.996 |
| 4 | 1.005 |
| 5 | 1.004 |
| 6 | 0.997 |
| X(avg) | 1.000 |
| Sn | 0.005 |

*Copper concentrations are determined by the alkaline precipitation method in References 1 and 2 which is a standard chemical analysis method for copper.

TABLE XIV. PRECISION OF 1.000-g/l CADMIUM STANDARD SOLUTION

| Replicate | Cadmium Conc. (g/l)* |
|---|---|
| 1 | 1.006 |
| 2 | 1.003 |
| 3 | 0.993 |
| 4 | 0.999 |
| 5 | 1.007 |
| 6 | 0.999 |
| X(avg) | 1.001 |
| Sn | 0.005 |

*Cadmium concentrations are determined by the alkaline precipitation method in References 1 and 2 which is a standard chemical analysis method for cadmium.

TABLE XV. PRECISION OF 1.000-g/l IRON STANDARD SOLUTION

| Replicate | Iron Conc. (g/l)* |
|---|---|
| 1 | 1.003 |
| 2 | 1.000 |
| 3 | 1.002 |
| 4 | 1.001 |
| 5 | 1.002 |
| 6 | 1.002 |
| X(avg) | 1.002 |
| Sn | 0.001 |

*Iron concentrations are determined by the alkaline precipitation method in References 1 and 2 which is a standard chemical analysis method for iron.

TABLE XVI. PRECISION OF 5-ppm COPPER STANDARD SOLUTION BY AA SPECTROMETRY

| Replicate | Absor. (AU) 5-ppm Copper |
|---|---|
| 1 | 0.256 |
| 2 | 0.254 |
| 3 | 0.258 |
| 4 | 0.259 |
| 5 | 0.258 |
| 6 | 0.255 |
| X(avg) | 0.257 |
| Sn | 0.002 |

TABLE XVII. PRECISION OF 2-ppm CADMIUM STANDARD SOLUTION BY AA SPECTROMETRY

| Replicate | Absor. (AU) 2-ppm Cadmium |
|---|---|
| 1 | 0.178 |
| 2 | 0.174 |
| 3 | 0.176 |
| 4 | 0.176 |
| 5 | 0.178 |
| 6 | 0.177 |
| X(avg) | 0.177 |
| Sn | 0.002 |

TABLE XVIII. PRECISION OF 5-ppm IRON STANDARD SOLUTION BY AA SPECTROMETRY

| Replicate | Absor. (AU) 5-ppm Iron |
|---|---|
| 1 | 0.199 |
| 2 | 0.195 |
| 3 | 0.197 |
| 4 | 0.198 |
| 5 | 0.196 |
| 6 | 0.200 |
| X(avg) | 0.198 |
| Sn | 0.002 |

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