AMMRC PTR 71-2

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DETERMINATION OF LOW COPPER IN STEELS AND IRONS BY ATOMIC ABSORPTION

EDNA F. JACOBSON
MATERIALS TESTING DIVISION

August 1971

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ARMY MATERIALS AND MECHANICS RESEARCH CENTER
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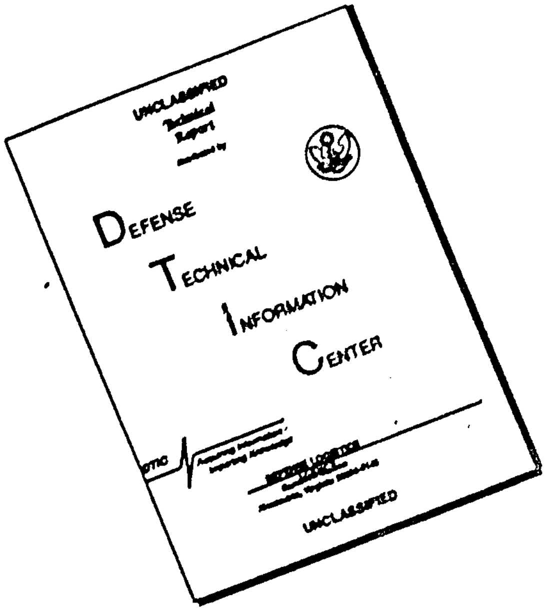

UNCLASSIFIED

Technical Report

DEFENSE

TECHNICAL

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Army Materials and Mechanics Research Center Watertown, Massachusetts 02172	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE
DETERMINATION OF LOW COPPER IN STEELS AND IRONS BY ATOMIC ABSORPTION

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Product Technical Report

5. AUTHOR(S) *(First name, middle initial, last name)*
Edna F. Jacobson

6. REPORT DATE August 1971	7a. TOTAL NO. OF PAGES 16	7b. NO. OF REFS 4
8a. CONTRACT OR GRANT NO. b. Project No. PEMA c. AMC Code No. 49310M6350 d.	9a. ORIGINATOR'S REPORT NUMBER(S) AMMRC PTR 71-2 9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*	

10. DISTRIBUTION STATEMENT
Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY U. S. Army Materiel Command Washington, D. C. 20315

13. ABSTRACT

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DD FORM 1 NOV 65 1473

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Iron alloys						
Copper steels						
Residual copper						
Chemical analysis						
Atomic absorption						

UNCLASSIFIED

Security Classification

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Product Technical Report by

EDNA F. JACOBSON

August 1971

Project PEMA
AMC Code 49310M6350
Materials Testing Technology

This project has been accomplished as part of the U. S. Army Manufacturing Methods and Technology Program, which has as its objective the timely establishment of manufacturing processes, techniques or equipment to insure the efficient production of current or future defense programs.

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An analytical method has been developed for the rapid determination of low copper (50 to 1800 parts per million) by atomic absorption. The method was successfully applied to different types of steels and irons, for example, low-alloy steel, stainless steel, tool steel, maraging steel, ingot iron, and cast iron. The detailed analytical method is appended to this technical report.

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ABSTRACT

I. INTRODUCTION

The determination of low copper in steels and irons is often required in quality assurance testing, research programs, and National Bureau of Standards cooperative certification. In electrogravimetric methods, large samples are required for low copper, many analytical separations have to be made, and the entire procedure is time-consuming. Photometric methods[1,2] do exist which are very reliable; however, most photometric methods for low concentrations require organic solvent extractions and the need for high grade chemicals in order to eliminate the problems of high blanks. The cuprizone photometric method[2] eliminates the need of solvent extraction, but duplicate samples must be run in order to compensate for background color, and the presence of high nickel (15 percent and over) and cobalt (25 percent and over) interferes. Therefore, this method would not be applicable to maraging steels (20 percent nickel) and some of the newer experimental alloys.

Copper can also be determined spectrographically, and reliable results can be obtained. But, many more manipulations are required after sample dissolution than is required by atomic absorption analysis, thus making the spectroscopic determination of copper more time-consuming and costly.

Methods for the determination of copper in steel and cast irons by atomic absorption have been published[3,4]. However, different instruments, burners, gas mixtures, and acid concentrations were used.

The atomic absorption method for copper developed under this study and appended to this report is very rapid. It is a direct method, that is, after dissolution of the sample in acid, the solution is diluted to volume, aspirated, and the copper content calculated. The only variation is in the presence of high silicon or tungsten, when a filtration after dissolution is required in order to avoid clogging of the aspirator.

Accurate results were obtained on 26 National Bureau of Standards samples including 16 steels, 1 maraging steel, 2 ingot irons, and 7 cast irons. In complex alloys, copper has been determined as easily as in a plain carbon steel.

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[1] ASTM Standards, Part 32, Chemical Analysis of Metals; Sampling and Analysis of Metal Bearing Ores, ASTM Designation: E 30-70, Standard Methods for Chemical Analysis of Steel, Cast Iron, Open-Hearth Iron and Wrought Iron, Copper by the Neocuproine Photometric Method, 1971, p. 71-73.

[2] MURRAY, W. K., *The Spectrophotometric Determination of Copper in Titanium and Other Metals with Dicyclohexanone Oxalydihydrazone*, Army Materials and Mechanics Research Center, WAL TR 401/229, May 1958.

[3] BEYER, M., *The Determination of Manganese, Copper, Chromium, Nickel, and Magnesium in Cast Iron and Steel*, Atomic Absorption Newsletter, v. 4, no. 3, 1965, p. 212-223.

[4] KINSON, K., and BELCHER, C. B., *The Determination of Minor Amounts of Copper in Iron and Steel by Atomic Absorption Spectrophotometry*, Anal. Chim. Acta, v. 31, 1964, p. 180-183.

II. EXPERIMENTAL

In order to determine the effect of the acid medium on sensitivity, three standard copper solutions were prepared, each containing the same amount of copper. The three different media were dilute nitric acid, dilute perchloric acid, and dilute hydrochloric-nitric acid mixture.

Setting the wavelength at 3247 Å, which is the most sensitive line for copper, the instrument was set at zero absorbance by aspirating water. The three copper standard solutions were aspirated and absorbance recorded. The dilute hydrochloric-nitric acid mixture improved the absorbance over the dilute nitric acid alone, while the dilute perchloric acid gave practically no absorbance reading. The combination of hydrochloric and nitric acids is most desirable as it permits the easy dissolution of many iron-base materials.

The next step was to establish the optimum instrumental parameters with the atomic absorption instrument used at AMMRC, that is, Jarrel-Ash 82-546. The parameters shown in Table I were established:

TABLE I. INSTRUMENTAL PARAMETERS FOR THE JARRELL-ASH INSTRUMENT

Total Consumption	
Burner Height	Scale Number 0
Fuel	Hydrogen
Pressure	24 psi
flow rate	85 scfh
Support Gas	Air
Pressure	30 psi
Flow Rate	25 scfh
Wavelength	3247 Å
Current	4 mA-Normal
Voltage	610
Damping	Full

A set of standard solutions containing from 0.2 to 5.0 μg of copper per milliliter was prepared and aspirated. A straight line following Beer's law was obtained (see Figure 1).

To study the effect of iron on the copper calibration curve, several lots of pure iron were tested. As much as 37 to 933 parts per million (ppm) of copper were found in the pure iron samples. Such material would seriously limit both the upper and lower parts of a calibration curve. A zone-refined iron was obtained and tested, and its copper content was found to be about 10 ppm. This level of copper could be conveniently tolerated. Figure 2 shows the effect of 1.0 and 0.50 g of iron on a typical calibration curve. The increased sensitivity of the 0.50 g of iron dictated the use of this amount in subsequent testing of National Bureau of Standards standard samples.

Over a range in which Beer's law applies, a linear relationship exists between the concentration and absorbance values. Accordingly, the slope of such a relationship can be used as a factor for converting absorbance values to concentration values and thus avoid the need for using calibration curves. Table II shows the factors obtained for one set of standard solutions which were added to the equivalent of 0.50-g samples of iron.

The averages of the factors obtained on other days were 10.26, 10.47, and 10.55. These can be considered to be in good agreement, but the slight differences indicate that a set of standards must be run from day to day in order to get the maximum reliability in analyzing unknowns.

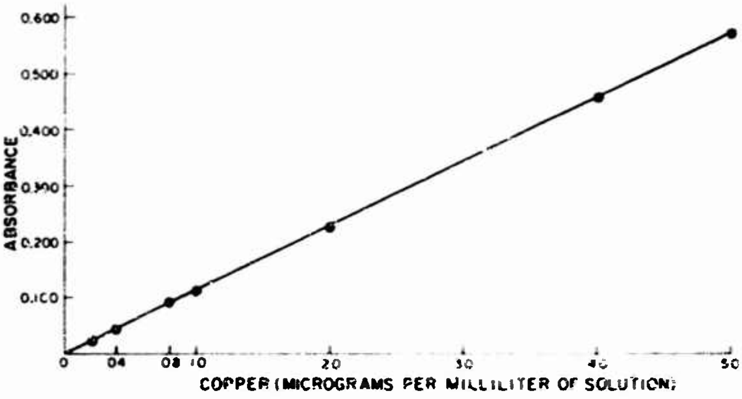

Figure 1. Calibration curve – copper in hydrochloric and nitric acids

TABLE II. CONFORMANCE TO BEER'S LAW

Copper µg/ml	Corrected Absorbance	Factor = $\frac{\mu g\ Cu/ml}{Absorbance}$
0.25	0.025	10.00
0.50	0.048	10.42
1.50	0.147	10.20
2.50	0.238	10.50
5.00	0.477	10.48
7.00	0.649	10.79
9.00	0.846	10.64
	Average	10.43

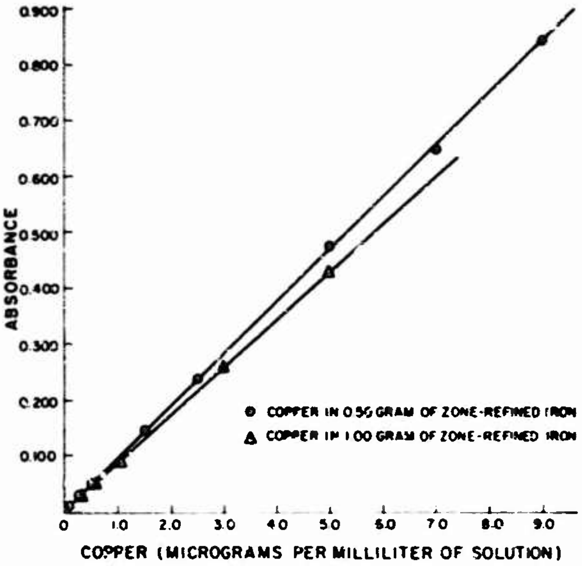

Figure 2. Calibration curve

III. TESTING OF NBS STANDARDS

In order to obtain information on accuracy and applicability to many types of ferrous materials, various NBS standard steels and irons were analyzed as unknowns. Because of the variety of materials tested, it would not be necessary to make a study of interfering elements, unless one particular type of material would produce results which were not comparable with the NBS certified values. Composition of the steels and irons used are shown in Tables III and IV, respectively.

TABLE III. COMPOSITION OF NBS STANDARD STEELS

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
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TABLE IV. COMPOSITION OF NBS STANDARD IRONS

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Preliminary tests were performed on two sets of cast iron samples, in order to determine which method of dissolution and filtering would be preferred. These samples must be filtered due to the high silica present, otherwise, clogging of the aspirator by the silica would occur. One set of cast irons was dissolved directly in the 100-ml volumetric flasks, diluted to volume, and then dry-filtered into another vessel. The second set of irons was dissolved in beakers, filtered into volumetric flasks, and then diluted to volume. Both sets of solutions were aspirated, and the results obtained (see Table V) indicated that either method was satisfactory. However, due to the high silica content, it is preferable to dissolve the sample in a beaker and then filter into a volumetric flask.

TABLE V. RESULTS FOR CAST IRONS BY DIFFERENT TECHNIQUES OF FILTERING

Sample No.	Filtering Before Dilution	Filtering After Dilution
7d (range 0.037-0.048)	0.041%	0.038%
7f (range 0.021-0.023)	0.021%	0.022%

(If a flask is used for the dissolution, it must be washed with ammonium hydroxide to remove the silica which adheres to the walls of the flask.)

A trial run was made on NBS standard sample 132a, which contains 6.2 percent tungsten, in order to see if any copper would be occluded or lost during the filtration of the tungstic oxide. The certified value is given as 0.120 percent copper with a range from 0.112 to 0.125 percent. The copper value obtained for this sample was 0.123 percent, indicating that this method could be used in the presence of high tungsten content. However, the tungstic oxide must be removed by filtration prior to the aspirating of the sample to avoid clogging of the aspirator.

The results obtained on the NBS Standard Samples are shown in Table VI for steels and Table VII for cast irons.

Some of the samples show duplicate results which were obtained on different portions of the samples and the copper content determined at different times. The results obtained by atomic absorption are calculated in percent so that the comparison between the NBS certified values and those found can be compared more easily. The difference in percent between the certified and found values is based on the certified values. The range shown is the lowest and highest values obtained by the various cooperators who had participated in the NBS standard cooperative testing program.

In reviewing the values found with the NBS certified values, the agreement can be considered excellent. The differences between the copper found values and the certified average values did not exceed 0.006 percent, except for sample 6d which differed by 0.008 percent. However, the range between the high and low results is greater in 6d than in any other standard sample listed. In all cases, except for one run of standard sample 12b, the results fall within the cooperators' range, and that one is 0.001 percent less than the lowest certified value.

The wide variety of material covered by these standards and the fact that only iron and copper were used for the preparation of the standard curve indicate that there is no interference from the many elements represented in the various types of metals used.

TABLE VI. COMPARISON OF RESULTS WITH NBS STANDARD STEEL SAMPLES

Sample No.	Type	Copper Range	Certified Average Copper, %	Copper Found, %	Difference Copper, %
10g	Carbon Steel	0.006-0.010	0.008	0.008 0.008	0.000 0.000
22b	Carbon Steel	0.007-0.012	0.009	0.006 0.007	-0.003 -0.002
11d	Carbon Steel	0.000-0.014	0.010	0.011 0.012	+0.001 +0.002
111b	Ni-Mo Steel	0.025-0.032	0.028	0.025 0.026	-0.003 -0.002
160	Cr-Ni-Mo Steel	0.047-0.060	0.053	0.047	-0.006
101	Stainless	0.050-0.062	0.055	0.057	+0.002
14e	Carbon Steel	0.065-0.080	0.072	0.071 0.073	-0.001 +0.001
73c	Stainless	0.077-0.082	0.080	0.082	+0.002
30e	Cr-V Steel	0.091-0.100	0.094	0.092	-0.002
153	Co-Mo-W Steel	0.091-0.110	0.099	0.100	+0.001
36a	Cr-Mo Steel	0.100-0.122	0.114	0.112	-0.002
132a	Mo-W-Cr-V Steel	0.118-0.125	0.120	0.124	+0.004
32e	Ni-Cr Steel	0.123-0.134	0.127	0.129	+0.002
19f	Carbon Steel	0.149-0.156	0.151	0.153 0.149	+0.002 -0.002
106a	Cr-Mo-Al Steel	0.149-0.166	0.156	0.152	-0.004
101d	Stainless	0.18-0.191	0.184	0.190	+0.006
1156	Maraging	---	0.025*	0.023 0.023	-0.002 -0.002

*This is a spectrographic standard and the average result was obtained from a Provisional Certificate; therefore, no range was available. This sample was analyzed at AMMRC by the Neocuproine Photometric Method[1] with values of 0.023, 0.024, and 0.022 percent copper found.

TABLE VII. COMPARISON OF RESULTS WITH NBS STANDARD IRON SAMPLES

Sample No.	Type	Copper Range	Certified Average Copper, %	Copper Found, %	Difference Copper, %
4e	Cast Iron	0.005-0.016	0.010	0.012	+0.002
7f	Cast Iron (High P)	0.021-0.023	0.021	0.021	0.000
55c	Ingot	---	0.040*	0.039 0.037	-0.001 -0.003
7d	Cast Iron (High P)	0.037-0.048	0.042	0.042	0.000
122c	Cast Iron	0.049-0.051	0.050	0.051	+0.001
55c	Ingot	---	0.065†	0.065 0.063	0.000 -0.002
82a	Ni-Cr Cast Iron	0.071-0.080	0.076	0.077	+0.001
107a	Ni-Cr-Mo Cast Iron	0.098-0.111	0.103	0.103	0.000
6d	Cast Iron	0.136-0.166	0.151	0.143	-0.008

*This average result was obtained from a Provisional Certificate; therefore, no range was available.

†The provisional certificate shows a value of 0.066 percent copper. The 0.065 present value is given as the certified value in the NBS Catalog of Standard Materials. The range is not known.

IV. DISCUSSION

The most accurate way to prepare a calibration curve (or factor) is by the procedure described earlier in the report; that is, by adding known amounts of copper standard solution to the base metal. However, the calibration curves prepared for atomic absorption analysis do not have the same repeatability as do curves prepared for spectrophotometric analysis. This is understandable, for small changes in instrumental parameters may cause significant variations in the repeatability of a calibration curve. Even slight clouding of the mirrors may go unnoticed and cause changes. Thus, to maintain the same conditions for the unknowns as are used for the standards, the unknowns must be run at the same time, or within a period of time in which no instrumental changes are made or required.

The suggested preparation of standard solutions is very practical when a large number of copper determinations are needed. However, if a copper value is occasionally requested, then the preparation of a complete set of standards can become costly. It would be more feasible to run NBS standards for the preparation of the calibration curve (or factor). Three standards, containing concentrations of copper at the very low, low or middle, and upper levels should provide a good calibration curve (or factor). In order to evaluate the feasibility of this technique, three NBS standard samples No. 10g, 111b, and 106a (0.008, 0.028, and 0.156 percent copper, respectively) were carried through the procedure, with NBS standard sample No. 10f (0.032 percent copper, range 0.030 to 0.037) treated as an unknown.

These standards do not have to be of the same type of material as the unknown. The three standards selected because of their copper concentration were a carbon steel, a nickel-molybdenum steel, and a chromium-molybdenum-aluminum steel. The standard steel treated as the unknown was a carbon steel. The net absorbances of the three standards were plotted and the curve was satisfactory (see Figure 3). The values obtained on NBS sample No. 10f were 0.033 and 0.033 percent, a difference of +0.001 percent from the certified value. However, if only one standard sample had been run in order to determine the factor for calculating the unknown, the results for 10f would be as shown in Table VIII.

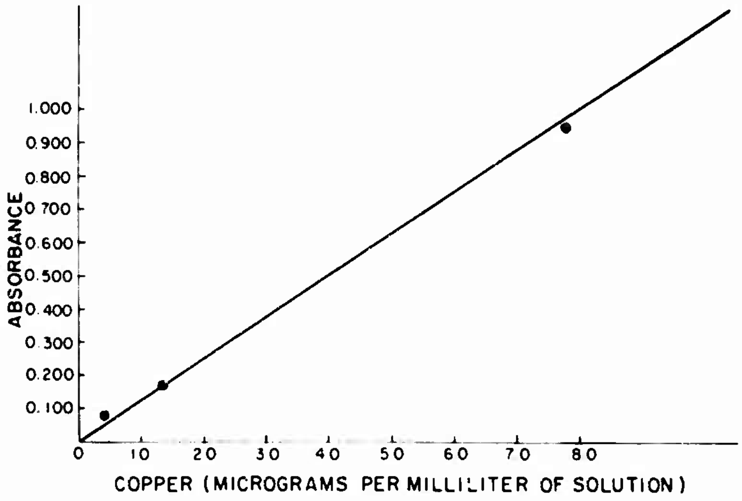

Figure 3. Calibration curve – using NBS standard samples

The results indicate that a slight bias can be obtained when calculating an unknown based on a single standard sample, particularly if the copper concentration is considerably above or below the amount present in the unknown.

One of the published methods[3], though similar in the dissolution and preparation of the sample, used a Perkin-Elmer instrument and different conditions. One of the main differences was in the manner of standardization, wherein only one standard was used, and that standard contained twice as much copper as the highest sample tested. Although a bias was evident, the deviations from the average certified values can be considered satisfactory for routine analysis.

As will be noted, the calibration curve obtained with the three NBS standard samples shows an increase in the slope in comparison with the previous calibration curve (Figure 2). This indicates that higher absorbance readings were obtained for the copper. This was not unexpected, since the mirrors were cleaned between the time of preparing the two calibration curves. This confirms how very important it is to obtain the calibration curve (or factor) under the same conditions as are used for the unknowns.

TABLE VIII. RESULTS FOR 107 BASED ON A FACTOR OBTAINED FROM A SINGLE STANDARD

Standard	Factor	Copper Found, %	Difference from Certified Value
10g	645.2	0.028	-0.004
111b	740.7	0.033	+0.001
160a	789.2	0.036	+0.004

In regard to spectrographic results vs atomic absorption results, the latter has produced reliable results with one more significant number, that is, ±0.001 percent.

V. CONCLUSION

The atomic absorption method for copper in the range from 50 to 1800 ppm developed at AMMRC and described in the Appendix is capable of producing accurate and precise results. It can be applied with equal ease to all types of steel including plain carbon steels, alloy steels, maraging steels, tool steels, and ingot iron and cast iron.

Because of its accuracy, rapidity, and simplicity, the method can be used for both routine and certification analysis. In addition, for routine analysis the preparation of a calibration curve (or factor) can be simplified by running as few as three NBS standard samples along with the unknowns.

VI. RECOMMENDATION

It is recommended that this method be used in appropriate military specifications covering the determination of copper in low-alloy steels, stainless steels, tool steels, maraging steels, and ingot iron and cast iron. And it is further suggested that this method be submitted to ASTM for consideration as a standard method.

APPENDIX

RECOMMENDED PROCEDURE FOR THE DETERMINATION OF COPPER IN STEELS, INGOT, AND CAST IRONS BY ATOMIC ABSORPTION

1. Scope

This method covers the determination of copper in concentrations from 50 to 1800 ppm.

2. Summary of Method

The sample is dissolved in hydrochloric and nitric acids. Any insoluble residue (silica or tungstic oxide) is filtered out, and the solution is diluted to a known volume. The solution is then aspirated using a total consumption burner with air and hydrogen as the oxidant and fuel, respectively. The micrograms of copper present in the sample is obtained from the calibration graph or by multiplying the absorbance by the factor obtained with the standard solutions.

3. Concentration Range

The recommended concentration range is from 0.1 to 0.9 µg of copper per milliliter of solution. This range may vary somewhat with different instruments.

4. Interferences

Interferences such as silica or tungstic oxide are removed by filtration in order to prevent clogging of the aspirator.

5. Apparatus

An atomic absorption spectrophotometer equipped with a copper hollow cathode tube and a total consumption burner that uses air and hydrogen.

6. Reagents

(a) Copper, Standard Solution A (1 ml = 100 µg Cu). Dissolve 0.1000 g of copper metal (purity: 99.9 percent minimum) in 10 ml of water and 15 drops of HNO_3. When dissolution is complete add 10 ml of HCl. Transfer to a 1-liter volumetric flask, dilute to volume with water, and mix.

(b) Copper, Standard Solution B (1 ml = 1 µg Cu). Using a pipet, transfer 2 ml of copper solution A to a 200-ml volumetric flask, dilute to volume with water, and mix. Prepare fresh as needed.

(c) Iron Solution (1 ml = 0.050 g Fe). Dissolve 10 g of iron metal (copper, 10 ppm maximum) in 80 ml of HCl (1+1). When dissolution is complete, add HNO_3 dropwise until the iron is oxidized. Boil gently until oxides of nitrogen are expelled. Cool, transfer to a 200-ml volumetric flask, dilute to volume with water, and mix.

7. Preparation of Calibration Curves (or Factors)

(a) For Umpire Analysis

Using pipets, transfer 0, 10, 30, and 50 ml of copper solution B (1 ml = 1 μg Cu) and 1, 3, 5, 7, and 9 ml of copper solution A (1 ml = 100 μg Cu) to 100-ml volumetric flasks containing 10 ml of iron solution (1 ml = 0.050g Fe), dilute to volume with water, and mix.

(b) For Routine Analysis

(1) Transfer 0.500-g samples of NBS Standard Samples No. 10g, 73c, and 106a*, weighed to the nearest 0.5 mg, to 150-ml beakers.

(2) Add 5 ml of HCl (1+1) and heat gently until dissolution is complete†, oxidize with 10 drops of HNO_3, and boil gently until oxides of nitrogen are expelled. Cool, add 10 ml of water, and bring to a boil. If silica or tungstic oxide is present, proceed to step (3); otherwise, transfer the solution to a 100-ml volumetric flask, dilute to volume with water, and mix.

(3) For solutions containing insoluble matter, add about 35 ml of water and bring the solution to a boil. If the insoluble matter is silica, filter through a 9-cm No. 41 paper; if it is tungstic oxide, filter through a double 9-cm No. 42 paper containing a small quantity of filter paper pulp. Collect the filtrate in a 100-ml volumetric flask. Wash the paper and residue about six times with hot water, cool, dilute to volume with water, and mix.

(4) Reagent Blank Solution. Carry a reagent blank through the entire procedure, using the same amounts of all reagents with the sample omitted.

(c) Photometry

(1) With the copper hollow cathode tube in position, energized and stabilized, locate the wavelength setting (in the vicinity of 3247 Å) that gives the maximum response of the detector system.

(2) Light the burner, allow it to reach thermal equilibrium, and adjust the instrument to zero absorbance while aspirating water. Aspirate the standard copper solution, or the NBS standard sample solution, with the highest concentration. Adjust the burner, the air and fuel pressures and their flow rates, and the position of the capillary to obtain maximum response. A pressure of 30 psi for air and 24 psi for hydrogen, at respective flow rates of 25 scfh and 85 scfh, produced maximum response with the total consumption burner used to develop this procedure.

(3) Aspirate the highest copper solution a sufficient number of times to establish that the absorbance is not drifting. Record six readings and calculate the standard deviation, s, of the readings as follows:

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*If the above standard samples are not available, select three standard samples that will yield about 0.5, 4.0, and 8.0 μg Cu/ml when dissolved and diluted as described in 7 (b) (2).

†For certain types of material, 3 to 5 drops of HNO_3 added to the solution will aid in the dissolution. However, a large excess of HNO_3 is to be avoided. For some high-alloy steels, 15 drops of HNO_3 will be required for complete oxidation of the sample solution.

$$s = (A-B) \times 0.40$$

where

A = the highest of the six values found, and

B = the lowest of the six values found.

(4) For umpire analysis, beginning with the iron solution to which no copper was added, aspirate each calibration solution in turn and record its absorbance. If the value for the highest copper solution differs from the average of the six values by more than twice the standard deviation, s, as determined in step (3), above, or more than 0.01 multiplied by the average of the six values, whichever is greater, repeat the measurement. If this value indicates a trend or drift, determine the cause (for example, deposits in the burner or clogged capillary), correct it, and repeat steps (2), (3), and (4).

(5) For routine analysis, use the same procedure as in step (4) but with the NBS standard sample solutions and the reagent blank solution.

(d) Calibration Curve (or Factor)

(1) For umpire analysis, subtract the absorbance found for the iron solution to which no copper was added from the value of each of the standard solutions.

(2) For routine analysis, subtract the absorbance found for the reagent blank solution from the value of each NBS standard sample solution.

(3) Plot the net absorbance values against micrograms of copper per milliliter or calculate the average factor as follows:

$$\text{Factor} = \frac{\text{micrograms of copper per milliliter}}{\text{net absorbance}} .$$

8. Procedure

(a) Test Solution. Transfer a 0.500-g sample, weighed to the nearest 0.5 mg, to a 150-ml beaker. Proceed as directed in 7(b)(2) and 7(b)(3).

(b) Reagent Blank Solution. Proceed as directed in 7(b)(4).

(c) Photometry. Check the instrument by aspirating the highest copper solution. If the absorbance value agrees with the value obtained previously, then proceed to aspirate the reagent blank and the test solutions, aspirating the highest copper solution after every fourth run. If the value of the copper solution does not agree with the previous value, the most likely sources of error will be deposits in the burner or clogged capillary tube. After cleaning the burner and capillary tube, rerun the copper solution. If the absorbance value agrees with the previous runs continue with the reagent blank and test solutions. If it does not agree, rerun the set of standard solutions and plot a new calibration curve (or calculate a new factor), and run the reagent blank and test solutions at the same time.

9. Calculation

Convert the net abosrbance values of the test solution to micrograms of copper per milliliter by means of the calibration curve or the average factor. Calculate the ppm of copper as follows:

$$\text{Copper, ppm} = \frac{A}{B} \times 100$$

where

A = micrograms of copper per milliliter, and

B = grams of sample represented in the final volume.