WADC TECHNICAL REPORT 54-45

COMPOSITE SPECTROPHOTOMETRIC PROCEDURES FOR THE ANALYSIS OF LOW-ALLOY STEELS AND OF ALUMINUM ALLOYS

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FOREWORD

This report was prepared by the Analysis and Measurements Branch and was initiated under Project No. 7360, "Materials Analysis and Evaluation Techniques" Task No. 73600, "Compositional Analysis", formerly RDO No. 616-11, "Procedures for Compositional Analysis of Aircraft Alloys", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Mr. S. B. Simmons acting as project engineer.

ABSTRACT

Individual procedures were combined into one composite scheme of analysis and adapted to Materials Laboratory Beckman DU Spectrophotometer. Optical densities of constituents in low-alloy steels and alloys of aluminum were determined from aliquot portions from one composite solution of one gram sample, and without any preliminary separations. The composite scheme for analysis of low-alloy steels is presented in Section I. Detailed procedures and calibration curves are also presented. The composite scheme for analysis of low-alloy aluminum alloys is presented in Section II. Calibration curves and detailed procedures are presented. Results of evaluation tests are presented in Section III, Tables 1 through 8. Methods were checked by numerous replicate determinations on synthetic samples and National Bureau of Standards samples. Results indicate that these methods and techniques will save man-hours in the analysis of low alloys of steel and aluminum.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research

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LIST OF ILLUSTRATIONS

Abbreviations Used

NBS	—	National Bureau of Standards
Aliq	—	Aliquots
F	—	factors
mg	—	milligrams
D	—	density(optical)
Mμ	—	Millimicrons

INTRODUCTION

There will be no attempt in this report to review, in detail, the fundamentals of these methods.

The development of spectrophotometric procedures for the analysis of low-alloy steels and of aluminum and its alloys was completed by the University of Texas, and is reported in detail in WADC Technical Report 52-246, performed under Contract No. AF 33(038)-23168. The work was initiated under Research and Development Order No. 616-11, administered by Materials Laboratory, with O. O. Srp acting as project engineer.

The object of this report is to establish and evaluate a reliable, rapid, composite scheme of spectrophotometric analysis for constituents in low-alloy steels and aluminum, from methods developed by the University of Texas, and to adapt this composite scheme to Materials Laboratory Beckman UD Spectrophotometer.

The spectrophotometric scheme of analysis for constituents in low alloy steels from one sample is presented in precise orderly steps in the first part of section one. This scheme saves reading time, computation time, and simplifies the analysis for all constituents. Detailed procedures and calibration curves are presented in the last part of section one.

The composite scheme of analysis for constituents of low alloy aluminum is presented in the same manner in section two.

The evaluation tests used to establish the reliability of the methods are shown in section three.

SECTION I

LOW-ALLOY STEELS 1.000 GRAM SAMPLE WEIGHT

DISSOLVE IN 20 MILLILITERS HNO_3 1:1 +20 MILLILITERS H_2O; DILUTE TO 200 MILLILITER VOLUME

CHROMIUM

1. Factors (F):

Aliquot	Factor
10 milliliters	2.033
20 milliliters	1.016

2. Ingredients:
   0.1% to 0.8%
   20 milliliter aliquot
   +9.5 milliliters
   $Fe(ClO_4)_2$
   0.8% to 1.6%
   10 milliliter aliquot
   +9.5 milliliters
   $Fe(ClO_4)_2$
3. Procedure:
   a. Add 20 milliliters $HClO_4$
   b. Evaporate to strong fumes
   c. Fume 4 to 6 minutes longer
   d. Cool rapidly
   e. Add 10 milliliters H_2O
   f. Dilute to 50 milliliters (volumetrically)
   g. Transfer portion to 10-mm cell
   h. Reduce remainder in volumetric flask with one drop of $Fe(ClO_4)_2$
   i. Use this portion as the blank
4. Density:
   Read at 380 Mμ

NICKEL

1. Factors (F):

Aliquot	Factor
10 milliliters	0.978
3 milliliters	3.260

2. Ingredients:
   0.1% to 0.8%
   10 milliliter aliquot
   0.8% to 2.5%
   3 milliliter aliquot
3. Procedure:
   a. Add 1 milliliter H_2SO_4 and H_3PO_4
   b. Add 5 milliliters ammonium citrate solution
   c. Add 5 milliliters iodine solution
   d. Add 10 milliliters dimethylglyoxime solution
   e. Dilute to 50 milliliters (volumetrically)
   f. Prepare blank
   g. Use identical aliquots
   h. Add 10 milliliters NH_4OH 1:1
   i. Add all reagents except dimethylglyoxime solution
   j. Color fades
   k. Five to ten minutes maximum wait period
4. Density:
   Read at 540 Mμ

PHOSPHORUS

1. Factors (F):

Aliquot	Factor
10 milliliters	0.1026
20 milliliters	0.0513

2. Ingredients:
   0.005% to 0.05%
   20 milliliter aliquot
   0.05% to 0.10%
   10 milliliter aliquot
3. Procedure:
   a. Add 5 milliliters $HClO_4$
   b. Fume to approximately 3 milliliters
   c. Cool
   d. Add 10 milliliters H_2O
   e. Add 15 milliliters sodium sulfite
   f. Boil for 1 minute
   g. Cool flask in ice-water bath
   h. Add 20 milliliters Am-Mo-Hyd-Sulfite solution
   i. Dilute to 50 milliliter volume
   j. Pipette 25 milliliters to test tube
   k. Digest 9 minutes on steam bath
   l. Cool
   m. Use undeveloped portion as blank
4. Density:
   Read at 820 Mμ

COPPER

1. Factors (F):

Aliquot	Factor
20 milliliters	1.0513

2. Ingredients:
   0.1% to 0.8%
   20 milliliter aliquot
3. Procedure:
   a. Add 25 milliliters Rochelle salt solution
   b. Test solution with pH meter
   c. Set limits between 11.3 and 12.3 with 10% NaOH
   d. Add 2 milliliters alpha-benzoinoxime solution
   e. Transfer to separatory funnel
   f. Add 30 milliliters chloroform
   g. Dry filter to 50 milliliter volumetric flask
   h. Repeat extraction with 10 milliliters chloroform
   i. Dilute to mark with chloroform
   j. Prepare blank
4. Density:
   Read at 440 Mμ

LOW-ALLOY STEELS 1.000 GRAM SAMPLE WEIGHT

DISSOLVE IN 20 MILLILITERS HNO_3 1:1 +20 MILLILITERS H_2O

DILUTE TO 200 MILLILITER VOLUME

MOLYBDENUM

1. Factors(F):

Aliquot	Factor
5 milliliters	0.528

2. Ingredients:
   0.01% to 0.4%
   5 milliliter aliquot
3. Procedure:
   a. Add 25 milliliters H_2SO_4 1:6
   b. Add 5 milliliters NaSCN solution
   c. Add 10 milliliters $SnCl_2$: $2H_2O$ solution
   d. Shake vigorously
   e. Add 25 milliliters butyl acetate (pipette)
   f. Shake vigorously for 1 minute
   g. Add 10 milliliters NaSCN solution
   h. Add 5 milliliters $SnCl_2$ solution
   i. Shake after each addition
   j. Allow liquids to settle and separate
   k. Discard lower layer
   l. Add 25 milliliters H_2SO_4 1:6
   m. Add 5 milliliters NaSCN
   n. Add 5 milliliters $SnCl_2$
   o. Shake after each addition
   p. Prepare blank
4. Density:
   Read at 468 Mμ

MANGANESE

1. Factors(F):

Aliquot	Factor
10 milliliters	4.516
20 milliliters	2.258

2. Ingredients:
   0.25% to 1.0%
   20 milliliter aliquot
   1.0% to 2.1%
   10 milliliter aliquot
3. Procedure:
   a. Add 0.3 gm potassium periodate
   b. Boil solution 5 minutes
   c. Cool
   d. Dilute to 100 milliliters (volumetrically)
   e. Transfer portion to 10-mm cell
   f. For blank destroy color with one drop of KNO_2
4. Density:
   Read at 526 Mμ

LOW-ALLOY STEELS 0.5000 GRAM SAMPLE WEIGHT

DISSOLVE IN 50 MILLILITERS HNO_2 1:4

DILUTE TO 250 MILLILITER VOLUME

SILICON

1. Factors(F):

Aliquot	Factor
25 milliliters	0.567

2. Ingredients:
   0.25% to 0.4%
   25 milliliter aliquot
3. Procedure:
   For Color -
   a. Pipette all reagents
   b. Pipette 25 milliliters aliquot
   c. Add 5 milliliters $NaMoO_4$: $2H_2O$
   d. Allow to set for 10 minutes
   e. Add 10 milliliters NaF solution
   For Blank -
   a. Pipette all reagents
   b. Pipette 25 milliliters aliquot
   c. Add 10 milliliters NaF solution
   d. Allow to set for 10 minutes
   e. Add 5 milliliters $NaMoO_4$: $2H_2O$
4. Density:
   Read immediately at 375 Mμ
   (Color Fades)

Determination of Molybdenum

Reagents:

Butyl acetate
Hydrochloric acid
Nitric acid
Perchloric acid
Stannous chloride: dissolve 300 gm of $SnCl_2 \cdot 2H_2O$ in 200 milliliters of HCl, and dilute to one liter.
Sulphuric acid 1:6
Sodium thiocyanate (10% aqueous solution)

Procedure:

Dissolve one gram sample in 20 milliliters HNO_3 1:1. Add 20 milliliters of H_2O to speed dissolution. Transfer to a 200 milliliter volumetric flask. For 0.01% to 0.4% Mo, take a 5 milliliter aliquot. Transfer a 5 milliliter aliquot to a separatory funnel. Add 25 milliliters of 1:6 sulphuric acid. Add 5 milliliters of sodium thiocyanate solution. Add 10 milliliters of stannous chloride solution, with good shaking after each addition. Add 25 milliliters of butyl acetate. Shake the mixture vigorously for about 30 seconds. Add 10 milliliters more sodium thiocyanate solution. Add 5 milliliters more stannous chloride solution, and again shake the solution vigorously for about 1 minute. Allow the liquid to stand until there is a good separation of the liquid layers. Draw off the lower layer and discard. To the solution in the separatory funnel add 25 milliliters 1:6 sulphuric acid, 5 milliliters of sodium thiocyanante solution, and 5 milliliters of stannous chloride solution. Shake the mixture well and allow to stand for good separation of layers. Draw off and discard lower layer. Transfer portion to 10-mm cell. Simultaneously with the treatment of the sample prepare a blank, starting with 25 milliliters of 1:6 sulphuric acid, and carry it through all the steps of the procedure. Read density at 468 Mμ.

Factor for percent molybdenum,

5 milliliter aliquot = 0.5276

Reagents:

Alpha-benzoinoxime; 5% solution in 10% sodium hydroxide solution
Chloroform
Nitric acid 1:1
Sodium hydroxide (10% aqueous solution)
Sodium potassium tartrate (Rochelle salt) 300 gm of $NaKC_4H_4O_6:4H_2O$

Procedure:

Dissolve one gram sample in 20 milliliter of HNO_3 1:1. Add 20 milliliters H_2O to speed dissolution. Transfer to 200 milliliters volumetric flask.
For 0.1% to 0.8% Cu, take a 20 milliliter aliquot.
Transfer a 20 milliliter aliquot to a 250 milliliter beaker. Add 25 milliliters of Rochelle salt solution. Test the solution with a pH meter. Slowly add sodium hydroxide solution until the pH meter is within the limits 11.3 to 12.3. Add 2 milliliters of alpha-benzoinoxime solution. Transfer the solution to a 150 milliliter separatory funnel. Add 30 milliliters of chloroform and shake the funnel vigorously for one or two minutes. Let the funnel stand until the liquid layers are well separated. Discard the chloroform lower layer containing the copper benzoinoximate through a small dry filter paper into a 50 milliliter volumetric flask. Repeat the extraction with 10 milliliters of chloroform as before. Add the chloroform solution to the main extract in the volumetric flask. Dilute with chloroform to the mark. Prepare a blank by carrying the reagent through all the steps of the procedure. Read density at 440 Mμ.

Factor for percent copper,

20 milliliter aliquot = 1.0455

Reagents:

Ammonium molybdate solution: 300 milliliters of H_2SO_4 to 400 milliliters of water. Cool, dissolve 20 gm of ammonium molybdate in sulphuric acid solution, and dilute with water to one liter.

Hydrazine sulfate solution: dissolve 1.5 gm of hydrazine sulfate in one liter of water.

Perchloric acid

Sodium sulfite solution: dissolve 100 gm of anhydrous sodium sulfite in water and dilute to one liter.

Ammonium-molybdate-hydrazine sulfate sodium sulfite reagent: dilute 25 milliliters of ammonium molybdate solution to 60 milliliters with water, add 10 milliliters of the hydrazine sulfate solution and 20 milliliters of the sodium sulfite solution, and dilute to 100 milliliters with water. This solution is not stable and must be prepared immediately before use.

Procedure:

Dissolve one gram sample in 20 milliliters of HNO_3 1:1. Add 20 milliliters of water to speed dissolution. **Dilute** to 200 milliliters in a volumetric flask.
For 0.005% P, take a 20 milliliter aliquot.
For 0.05% to 0.10% P, take a 10 milliliter aliquot.
Transfer a suitable aliquot to a 125 milliliter Erlenmeyer flask. Add 5 milliliters of perchloric acid. Fume until the acid condenses freely in the neck of the flask, and continue to fume solution down to approximately 3 milliliters. Cool the solution. Add 10 milliliters of water and 15 milliliters of sodium sulfite solution. Boil solution one minute. Cool immediately in ice-water bath. Add 20 milliliters of ammonium molybdate hydrazine sulfate sodium sulfite solution. Transfer to a 50 milliliter volumetric flask. Dilute to mark with water. Pipette 25 milliliters of the solution to a large test tube and immerse it in boiling water for exactly 9 minutes to develop color. Cool to room temperature. Use undeveloped portion for blank. Read density at 820Mμ.

Factors for percent phosphorus are as follows:

10 milliliter aliquot = 0.1026

20 milliliter aliquot = 0.0513

Determination of Nickel

Reagents:

Ammonium citrate solution: dissolve 540 gm of solid in water and dilute to one liter.
Ammonium hydroxide 1:1
Dimethylglyoxime 0.1% ammonical solution: dissolve 1 gm of dimethylglyoxime in 500 milliliters of concentrated ammonium hydroxide and dilute to one liter.
Iodine solution: dissolve 8 gm of potassium iodide and 2.6 gm of iodine in water and dilute to one liter.
Nitric acid
Sulphuric-phosphoric acid mixture: to 850 milliliters of water add 75 milliliters of sulphuric acid and 75 milliliters of phosphoric acid.

Procedure:

Dissolve one gram sample in 20 milliliters HNO_3 1:1. Add 20 milliliters water to speed dissolution. Transfer to 200 milliliter volumetric flask.
For 0.1% to 0.8% Ni, take a 10 milliliter aliquot.
For 0.8% to 1.6% Ni, take a 3 milliliter aliquot.
Transfer a suitable aliquot to a 50 milliliter volumetric flask. Add the following reagents in order given with a good mixing after each addition: 1 milliliter of sulphuric-phosphoric acid mixture, 5 milliliters of ammonium citrate solution, 5 milliliters of iodine solution, 10 milliliters of dimethylglyoxime solution, and dilute with water to volume. Treat another identical aliquot with the same reagents except use 10 milliliters of 1:1 ammonium hydroxide instead of dimethylglyoxime. This portion serves as the blank. Read density at 540 Mμ.

Factors for percent nickel are as follows:

10 milliliter aliquot = 0.9780
3 milliliter aliquot = 3.2600

Determination of Chromium

Reagents:

Nitric acid 1:1
Perchloric acid (70%)
Ferrous perchlorate solution (32 gm $Fe(ClO_4)_2 + 6H_2O$)
dissolve in water and dilute to 500 milliliters volume.
1 milliliter = 0.10 gm Fe.

Procedure:

Dissolve one gram sample in 20 milliliters of HNO_3 1:1. Add 20 milliliters of water to speed dissolution. Transfer to 200 milliliter volumetric flask and dilute with water to mark.

For 0.1% to 0.8% Cr, take a 20 milliliter aliquot and add 9 milliliters of ferrous perchlorate solution.

For 0.8% to 1.6% Cr, take a 10 milliliter aliquot and add 9.5 milliliters of ferrous perchlorate solution.

Transfer suitable aliquot to a 500 milliliter Erlenmeyer flask and add 20 milliliters of perchloric acid. Evaporate to strong fumes of perchloric acid, and continue to heat for 2 to 6 minutes after fumes have cleared body of flask. Cool mixture immediately by swirling flask in a pan of cold water until solution solidifies; then add 10 milliliters of distilled water to the flask. Transfer solution to a 50 milliliter volumetric flask and dilute to volume.

Transfer portion to 10-mm cell. For blank, reduce the remainder in the volumetric flask with one drop of ferrous perchlorate solution. Read density at 380 Mμ.

Factors for percent chromium are as follows:

10 milliliter aliquot = 2.0328
20 milliliter aliquot = 1.0164

Determination of Manganese

Reagents:

Ammonium persulfate $(NH_4)_2S_2O_8$
Nitric acid 1:1
Phosphoric acid
Potassium nitrite (2% aqueous solution)
Potassium periodate

Procedure:

Dissolve one gram sample in 20 milliliters of HNO_3 1:1. Add 20 milliliters of H_2O to speed dissolution. Transfer to a 200 milliliter volumetric flask and dilute to volume.

For 0.25% to 1.0% Mn, take a 20 milliliter aliquot.
For 1.0% to 2.1% Mn, take a 10 milliliter aliquot.

Transfer suitable aliquot to a 250 milliliter beaker. Add 10 milliliters of phosphoric acid and 0.3 gm of potassium periodate. Boil the mixture for about 5 minutes to oxidize the manganese to permanganate. Cool the solution. Transfer it quantitatively to a 100 milliliter volumetric flask, and dilute to volume with water. Transfer portion to 10-mm cell. Destroy the purple color of another portion with one or two drops of potassium nitrite solution. Use this portion as the blank. Read the density at 526 Mμ.

Factors for percent manganese are as follows:

10 milliliter aliquot = 4.5160
20 milliliter aliquot = 2.2580

Determination of Silicon

Reagents:

Nitric acid
Potassium persulfate (saturated solution 8%)
Sodium fluoride (2.4% aqueous solution)
Sodium molybdate 12%

Procedure:

Dissolve 0.5 gram sample in 50 milliliters of HNO_3 1:4. Add 10 milliliters of potassium persulfate. Boil solution until clear. Cool flask and contents. Transfer contents to a 250 milliliter volumetric flask, and dilute to mark with water. Transfer 25 milliliter aliquots to a dry beaker or flask. One portion is to be used for the blank. To the 25 milliliter blank solution add 10 milliliters of sodium fluoride solution. To the 25 milliliter sample solution add 5 milliliters of sodium molybdate solution. After 10-minute wait, add 5 milliliters of sodium molybdate solution to the blank and 10 milliliters of sodium fluoride solution to the sample.

If slight turbidity appears, it usually disappears in 2 to 3 minutes. Read density at 375 Mμ immediately, for the silicon color fades.

Factor for percent silicon:

25 milliliter aliquot = 0.5670

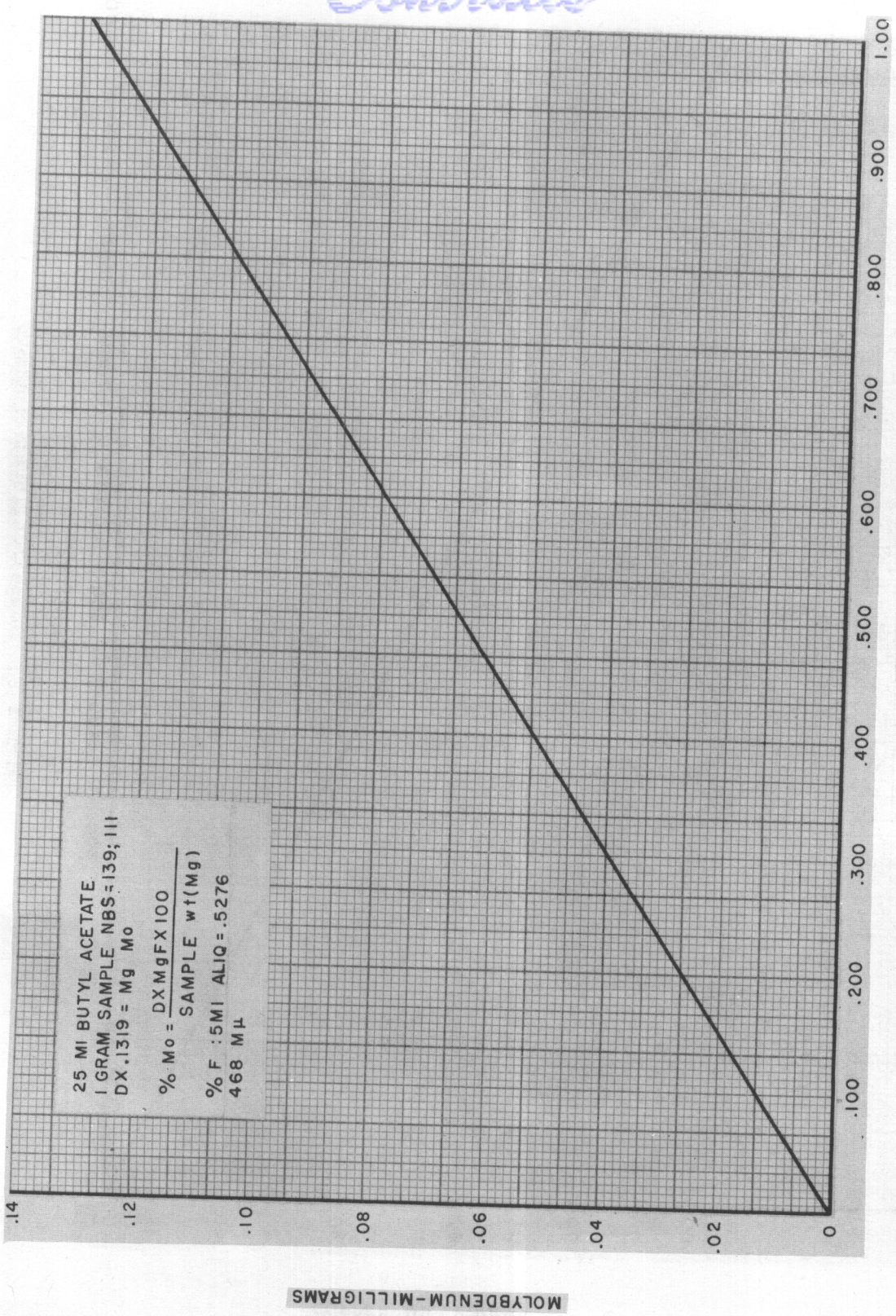

Figure 1. Molybdenum Calibration Curve

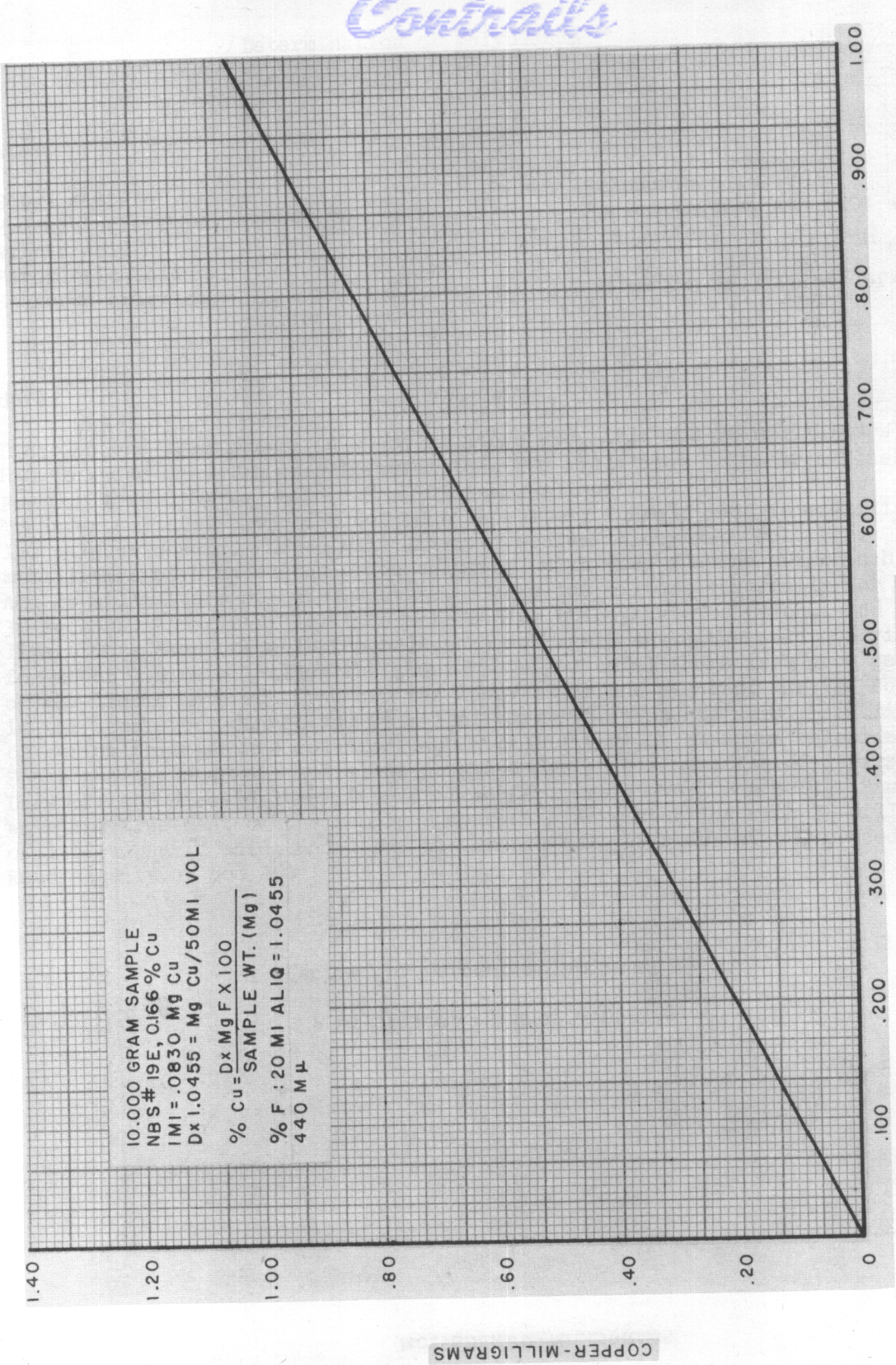

Figure 2. Copper Calibration Curve

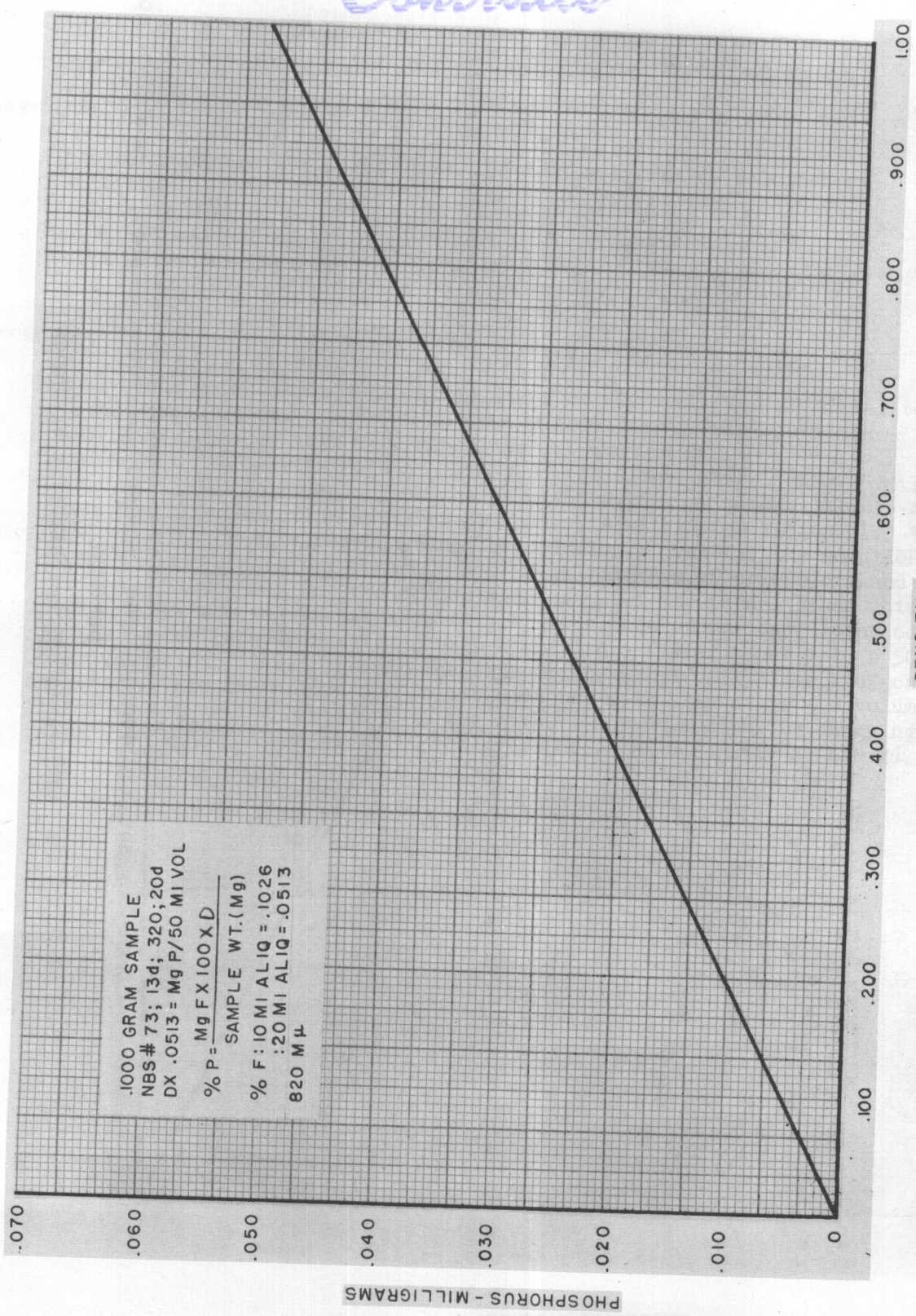

Figure 3. Phosphorus Calibration Curve

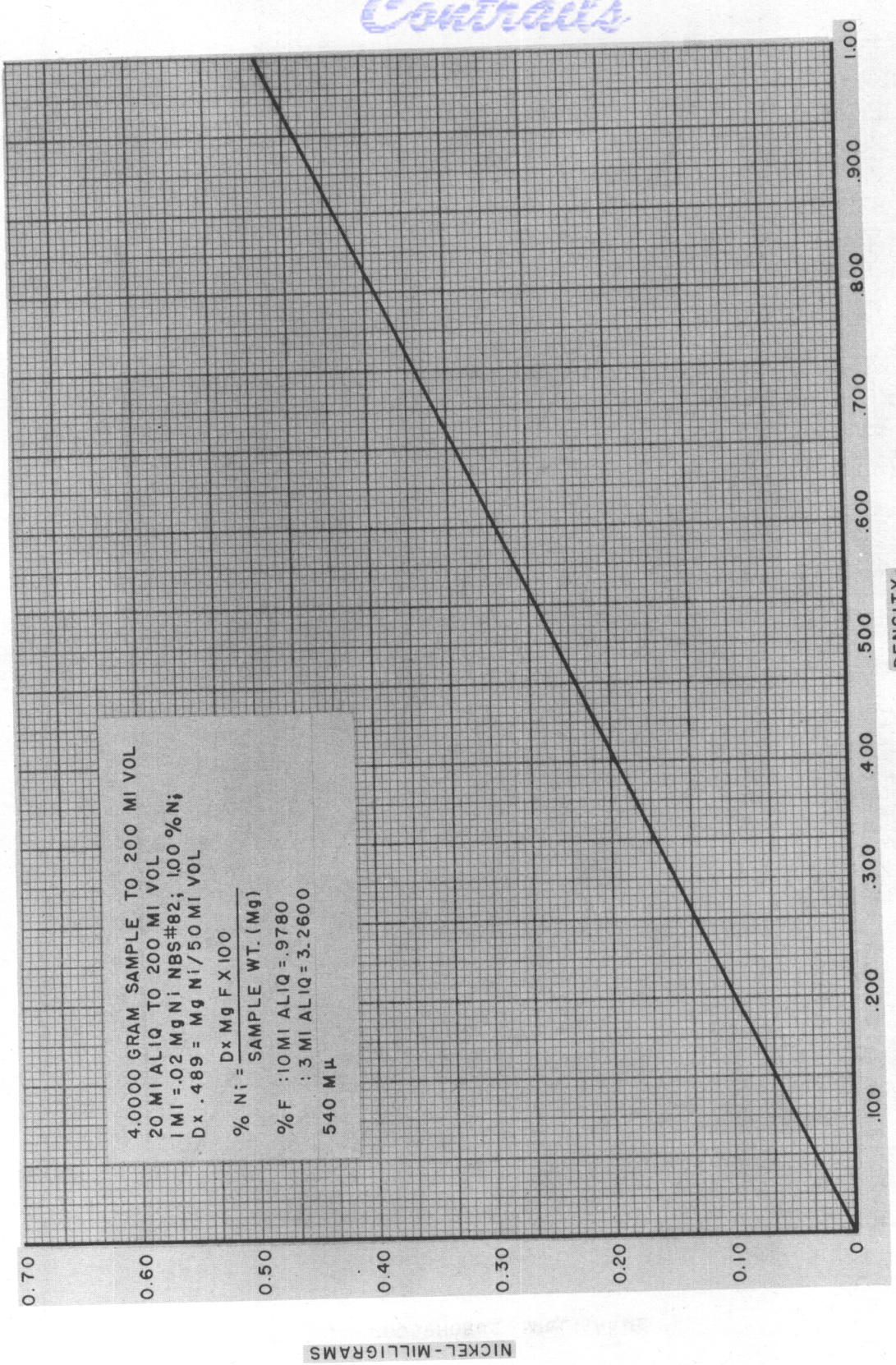

Figure 4. Nickel Calibration Curve

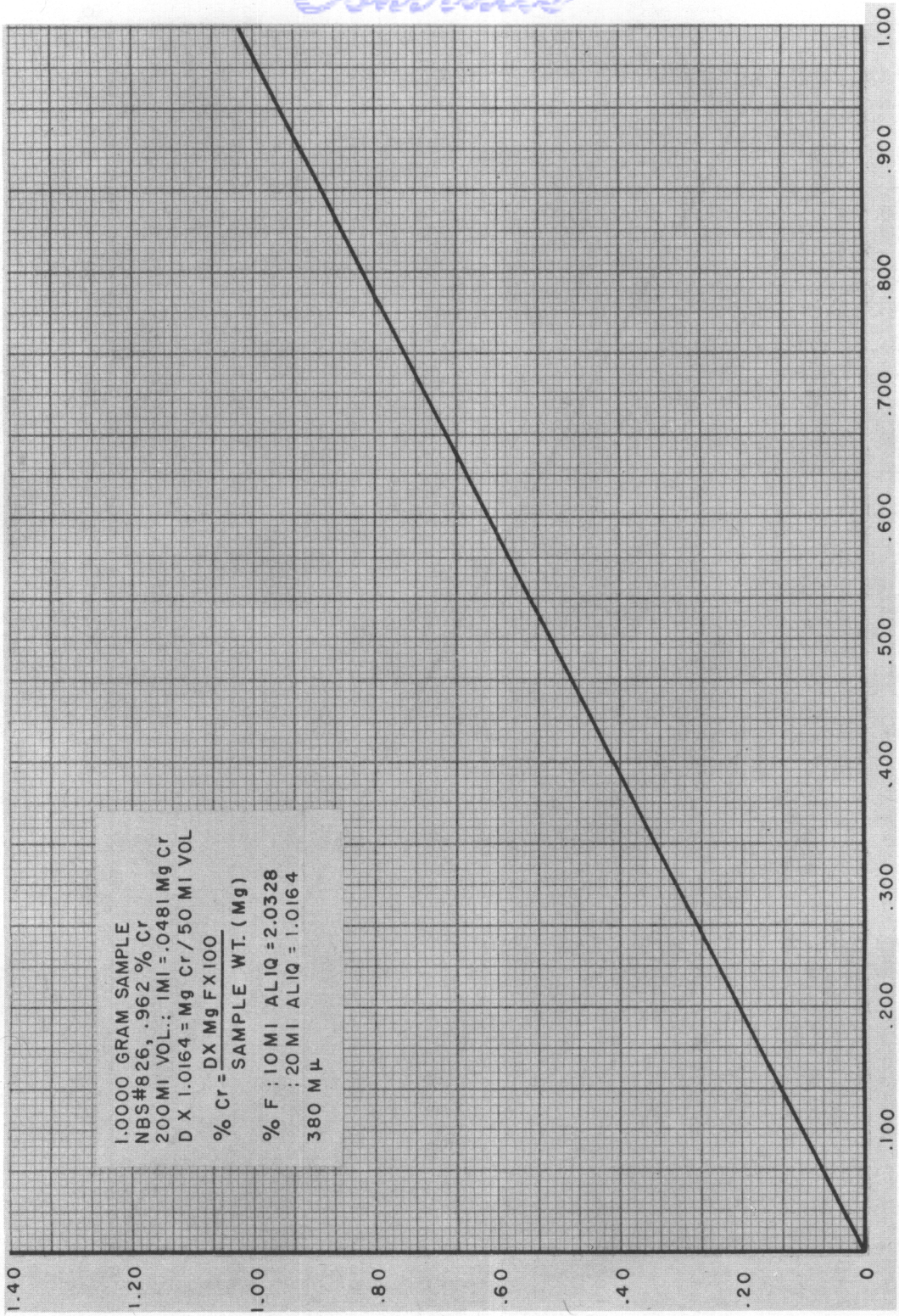

Figure 5. Chromium Calibration Curve

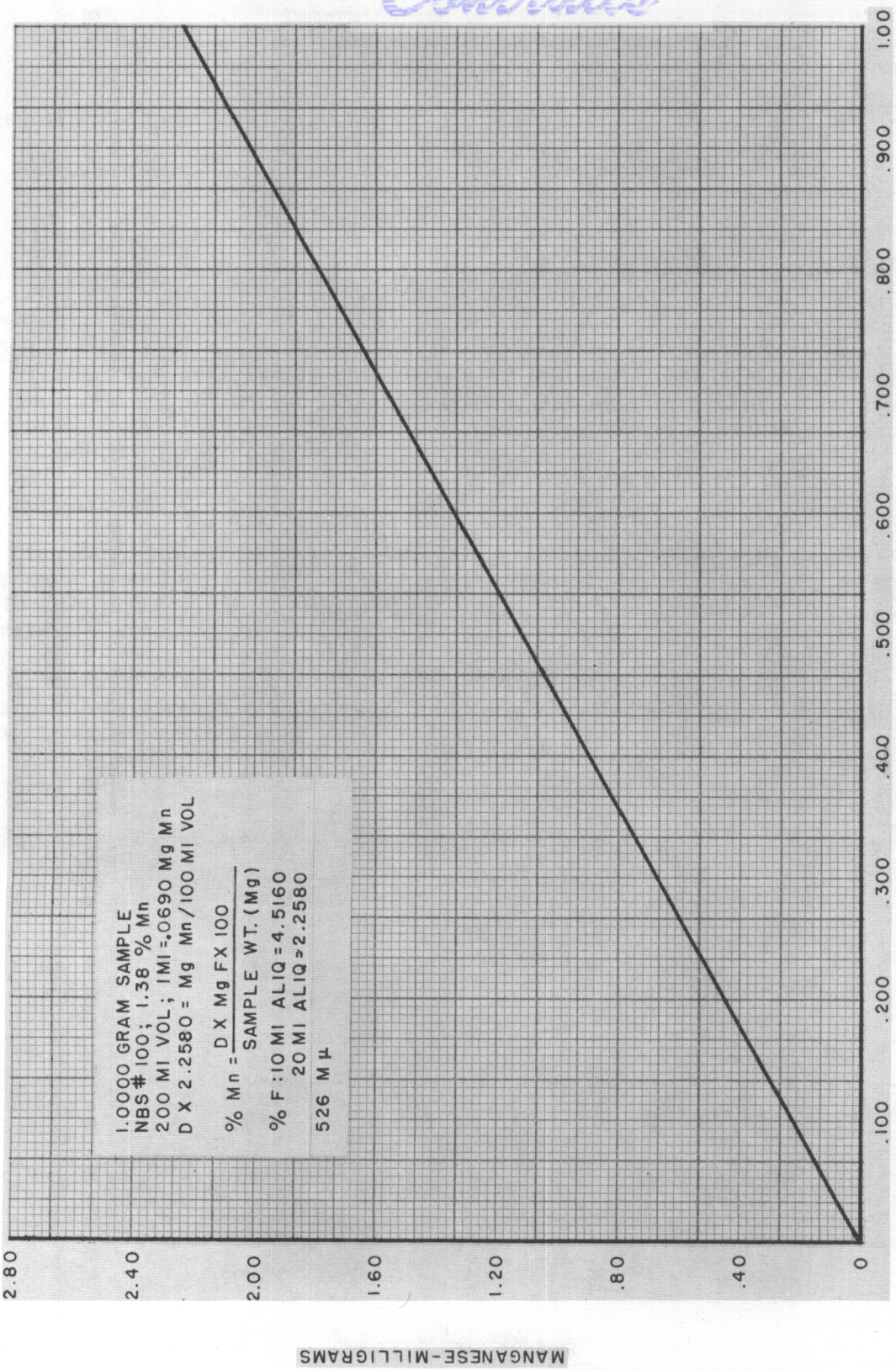

Figure 6. Manganese Calibration Curve

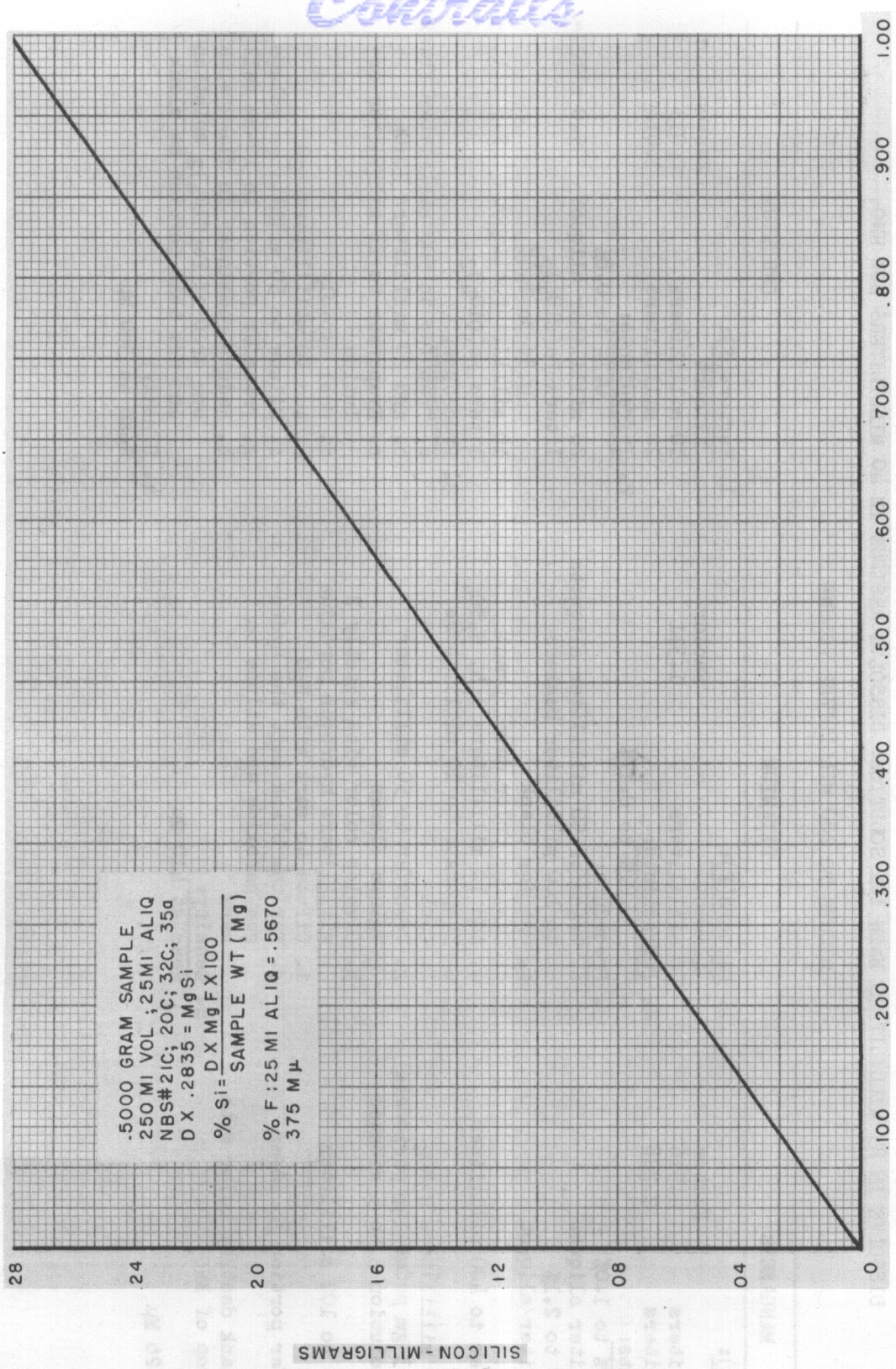

Figure 7. Silicon Calibration Curve

SECTION II

ALUMINUM ALLOYS 1.000 GRAM SAMPLE WEIGHT

DISSOLVE IN 25 MILLILITERS NaOH 10% SOLUTION; DISSOLVE RESIDUE IN 40 MILLILITERS HOT HNO_3

DILUTE TO 200 MILLILITER VOLUME

MANGANESE

1. Factors(F):

Aliquot	Factor
10 milliliters	4.516
20 milliliters	2.258

2. Ingredients:
   0.25% to 1.0%
   20 milliliter aliquot
   1.0% to 2.1%
   10 milliliter aliquot
3. Procedure:
   a. Transfer to 400 milliliter beaker
   b. Add 10 milliliters H_3PO_4
   c. Add 0.3 gm potassium periodate
   d. Boil solution 3 to 5 minutes
   e. Cool
   f. Dilute to 100 milliliter volume
   g. Transfer portion to 10-mm cell
   h. For blank destroy color with one drop of KNO_2
4. Density:
   Read at 526 Mμ

TITANIUM

1. Factors(F):

Aliquot	Factor
50 milliliters	1.311

2. Ingredients:
   0.01% to 0.17%
3. Procedure:
   a. Transfer 50 milliliter aliquots to 100 milliliter beakers
   b. One for blank
   c. One for color development
   d. Add 10 milliliters 1:4, H_2SO_4
   e. Evaporate to 10 milliliters
   f. Cool
   g. Transfer to 50 milliliter volume flasks
   h. Develop color with exactly 2 milliliters hydrogen peroxide
   i. Dilute to mark with H_2O
   j. For the blank omit the hydrogen peroxide and dilute to mark
4. Density:
   Read at 410 Mμ

CHROMIUM

1. Factors(F):

Aliquot	Factor
10 milliliters	2.033
20 milliliters	1.016

2. Ingredients:
   0.1% to 0.8%
   20 milliliter aliquot 9.0 milliliters $Fe(ClO_4)_2$
   0.8% to 1.6%
   10 milliliter aliquot 9.5 milliliters $Fe(ClO_4)_2$
3. Procedure:
   a. Transfer to 500 milliliter flask
   b. Add 20 milliliters $HClO_4$
   c. Evaporate to 18 milliliter solution
   d. Cool rapidly
   e. Add 10 milliliters H_2O
   f. Dilute to 50 milliliter volume
   g. Transfer portion to 10-mm cell
   h. Reduce remainder in flask with one drop of $Fe(ClO_4)_2$ solution and use this portion as blank
4. Density:
   Read at 380 Mμ

NICKEL

1. Factors(F):

Aliquot	Factor
10 milliliters	0.978
3 milliliters	3.260

2. Ingredients:
   0.1% to 0.8%
   10 milliliter aliquot
   0.8% to 1.6%
   3 milliliter aliquot
3. Procedure:
   a. Copper interferes with color development
   b. Add 3 milliliters H_2S solution to a 10 milliliter aliquot
   c. Add 10 drops H_2S solution to a 3 milliliter aliquot
   d. Dilute to 100 milliliters-filter
   e. Boil filtrate until odor of H_2S is removed
   f. Transfer to a 50 milliliter volumetric flask
   g. Add following reagents in order given with good mixing after each addition:
      1 milliliter H_2SO_4 and H_3PO_4 solution
      5 milliliters ammonium citrate solution
      5 milliliters iodine solution
      10 milliliters dimethylglyoxime solution
   h. Dilute with H_2O to volume
   i. Prepare blank using all reagents except dimethylglyoxime (instead use 10 milliliters NH_4OH 1:1)
   j. Color fades
4. Density:
   Read at 540 Mμ

IRON

Standard Method

1. Factors(F):

Aliquot	Factor
5 milliliters	4.018
10 milliliters	1.004

2. Ingredients:
   0.1% to 0.9%
   25 milliliter aliquot
3. Procedure:
   a. Transfer 25 milliliter aliquot to 100 milliliter beaker
   b. Add 2 gm lead
   c. Heat and stir to precipitate copper and filter
   d. Dilute filtrate to 100 milliliters volumetrically
   e. Take 5 milliliter aliquot portions; one for blank, one for sample
   f. Transfer to 50 milliliter volumetric flasks
   g. Add reagents in order given:
      2 milliliters hydroxylamine hydrochloride solution
      5 milliliters acetate buffer solution
      5 milliliters ortho-phenanthroline solution
      Do not add ortho-phenanthroline to blank
   h. Dilute to mark
4. Density:
   Read at 510 Mμ

Alternate Method

1. Factors(F):

Aliquot	Factor
5 milliliters	4.018
10 milliliters	1.004

2. Ingredients:
   0.1% to 0.5%
   50 milliliter aliquot
3. Procedure:
   a. Transfer 50 milliliter aliquot to 100 milliliter beakers
   b. Add 2 gm lead
   c. Boil, stir, and filter
   d. Dilute filtrate to 100 milliliters
   e. Take a 10 milliliter aliquot and transfer to 50 milliliter beakers
   f. Neutralize solution, drop by drop, with NH_4OH
   g. Acidify solution, drop by drop, with HNO_3 to the disappearance of precipitate
   h. Add exactly 2 drops in excess
   i. Transfer to 50 milliliter volumetric flask and continue to the determination of iron, as in standard method
4. Density:
   Read at 510 Mμ

Determination of Chromium

Reagents:

Nitric acid
Perchloric acid
Ferrous perchlorate solution (dissolve 325 gm $Fe(ClO_4)_2 \cdot 6H_2O$ in water and dilute to 500 milliliter volume) 1 milliliter = 0.10 gm Fe.
NaOH (10% solution)

Procedure:

Dissolve one gram sample of aluminum alloy in the usual manner with 25 milliliters of NaOH solution. Dilute to 200 milliliters, let settle, filter, and dissolve the residue with 40 milliliters of hot nitric acid. Transfer and dilute to 200 milliliters in a volumetric flask.

For 0.1% to 0.8% Cr, take a 20 milliliter aliquot and add 9 milliliters of ferrous perchlorate solution.
For 0.8% to 1.6% Cr, take a 10 milliliter aliquot and add 9.5 milliliters of ferrous perchlorate solution.

Transfer a suitable aliquot to a 500 milliliter Erlenmeyer flask, and add 20 milliliters of perchloric acid. Evaporate to strong fumes of perchloric, and continue to evaporate to approximately 18 milliliters of solution. Cool mixture immediately by swirling flask in pan of ice-cold water until solution solidifies. Then add 10 milliliters of water to flask. Transfer solution to 50 milliliter volumetric flask, and dilute to mark. Transfer a portion to a 10-mm cell. For the blank, destroy the remainder in the flask with one drop of ferrous perchlorate solution.

Read density at 380 Mμ.

Factors for percent chromium are as follows:
10 milliliter aliquot = 2.0328
20 milliliter aliquot = 1.0164

Determination of Manganese

Reagents:

Phosphoric acid
Potassium nitrate (2% aqueous solution)
Potassium periodate Meta KIO_4
Nitric acid
NaOH (10% solution)

Procedure:

Dissolve one gram sample of aluminum alloy in the usual manner with 25 milliliters of NaOH solution. Dilute to 200 milliliters, let settle, filter, and dissolve the residue in 40 milliliters of hot nitric acid. Transfer and dilute to 200 milliliters in a volumetric flask.

For 0.25% to 1.0% Mn take a 20 milliliter aliquot.
For 1.0% to 2.1% Mn take a 10 milliliter aliquot.

Transfer a suitable aliquot to a 400 milliliter beaker. Add 10 milliliters of phosphoric acid and .3 gm of potassium periodate. Boil the mixture 3 to 5 minutes to fully oxidize the manganese to permanganate. Cool the solution. Transfer it to a 100 milliliter volumetric flask, and dilute the volume with water. Transfer a portion to a 10-mm cell. Destroy the purple color of another portion with one or two drops of potassium nitrite solution. Use this portion as the blank.

Read density at 526 Mu
Factors for percent manganese are as follows:
10 milliliter aliquot = 4.5160
20 milliliter aliquot = 2.2580

Determination of Nickel

Reagents

Nitric acid
Ammonium citrate (540 gm dissolved in water and dilute to one liter)
Ammonium hydroxide 1:1
Dimethylglyoxime 0.1% ammonical solution (1 gm of dimethylglyoxime in 500 milliliters of NH_4OH; diluted to one liter)
Iodine solution (8 gm of potassium iodide and 2.6 gm of iodine in water diluted to one liter)
Sulphuric and phosphoric acid mixture (to 850 milliliters of water add 75 milliliters of H_2SO_4 and 75 milliliters of H_3PO_4)
H_2S solution (3% NH_4OH, saturated with H_2S)

Procedure:

Dissolve one gram of aluminum alloy sample in the usual manner with 25 milliliters of NaOH solution. Dilute to 200 milliliters, let settle, filter, and dissolve the residue in 40 milliliters of hot nitric acid. Transfer and dilute to 200 milliliters in a volumetric flask.

For 0.1% to 0.8% Ni, take a 10 milliliter aliquot.
For 0.8% to 1.6% Ni, take a 3 milliliter aliquot.

Copper interferes with the development of the nickel color. If copper is present, transfer a suitable aliquot to a 250 milliliter beaker. Add 3 milliliters of H_2S solution to a 10 milliliter aliquot, and 10 drops to a 3 milliliter aliquot. Filter, and dilute filtrate to 100 milliliters. Boil the solution until the odor of H_2S is removed. Transfer to a 50 milliliter volumetric flask, and add the following reagents in order given, with good mixing after each addition:

1 milliliter of H_2SO_4 and H_3PO_4 solution.
5 milliliters of ammonium citrate solution.
10 milliliters of dimethylglyoxime solution.
Dilute to volume with water.

Treat another identical aliquot in the same manner except do not add dimethylglyoxime; add 10 milliliters of NH_4OH 1:1 solution instead; use this portion as the blank

Read density at 540 Mμ. Read immediately, as color fades. One to three minutes maximum wait period.

Factors for percent nickel are as follows:

10 milliliter aliquot = 0.9780

3 milliliter aliquot = 3.2600

Reagents:

Acetate buffer mixture (140 gm sodium acetate trihydrate in water and 60 milliliters of glacial acetic acid; dilute to one liter)
Hydroxylamine hydrochloride (1% aqueous solution)
Ortho-phenanthroline (2% aqueous solution) (or 1-10 phenanthroline)
Granular lead metal
Nitric acid
NaOH (10% solution)

Procedure:

Method "A"

Dissolve one gram sample of aluminum alloy in the usual manner with 25 milliliters of NaOH solution. Dilute to 200 milliliters, let settle, filter, and dissolve the residue in 40 milliliters of hot nitric acid. Transfer and dilute to 200 milliliters in a volumetric flask.

Transfer 25 milliliter aliquots to 100 milliliter beakers. Add 2 gm of lead (iron free). Heat the solution, and stir often to precipitate the copper. Cool, and filter off the copper and lead. Receive the filtrate directly into a 100 milliliter volumetric flask. Dilute to volume with water. Transfer identical 5 milliliter aliquot portions of this solution to 50 milliliter volumetric flasks. One is for the blank, and one is for the measurement of the iron color. Add the following reagents in order given, but do not add ortho-phenanthroline to the blank.

2 milliliters of hydroxylamine hydrochloride solution.
5 milliliters of acetate buffer mixture solution.
5 milliliters of ortho-phenanthroline solution.

Dilute to mark with water. Read density at 510 Mμ. Factor for 5 milliliters = 4.0176.

Method "B"

For 0.1% to 0.5% Fe:

Transfer 50 milliliter aliquots to 100 milliliter beakers. Add 2 gm of lead. Heat with frequent stirring to precipitate copper. Filter off the lead and copper. Dilute filtrate to 100 milliliter volume. Transfer 10 milliliter aliquots to 50 milliliter beakers, and neutralize the solution drop by drop with NH_4OH. Then, drop by drop, reacidify the solution with nitric acid, just to the disappearance of the precipitate, and add exactly 2 drops in excess. Transfer solution to 50 milliliter volumetric flasks, and continue determination of iron as in method "A".

Factor for 10 milliliter aliquot = 1.0044

Determination of Titanium

Reagents:

Hydrogen peroxide 3%
Sulphuric acid 1:4
NaOH 10% solution
Nitric acid

Procedure:

Dissolve one gram sample of aluminum alloy in the usual manner with 25 milliliters of NaOH solution. Dilute to 200 milliliters, let settle, filter, and dissolve the residue in 40 milliliters of hot nitric acid. Transfer and dilute to 200 milliliters in a volumetric flask.

For 0.01% to 0.17% Ti:

Transfer identical 50 milliliter aliquots to 100 milliliter beakers; one for color development, and one for the blank. Add 10 milliliters of 1:4 H_2SO_4. Evaporate to approximately 10 milliliter volume. Cool, and transfer to 50 milliliter volumetric flasks.

To develop color, add exactly two milliliters of hydrogen peroxide. Mix thoroughly, and dilute to mark with water. For the blank, omit the hydrogen peroxide, and dilute to volume with water.

Read density at 410 Mμ.

Factor for percent titanium = 1.3108

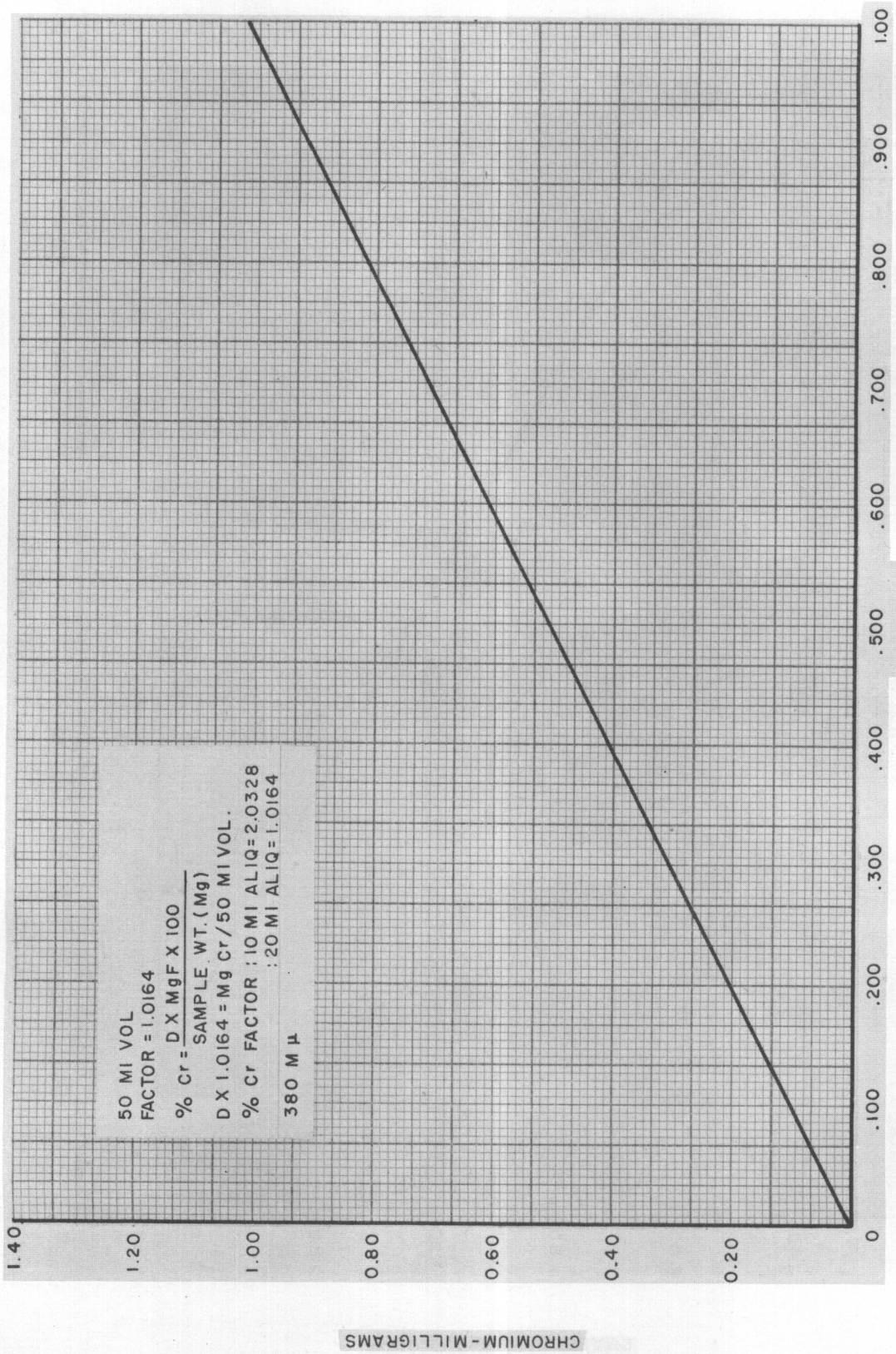

Figure 8. Chromium Calibration Curve (Aluminum Alloy)

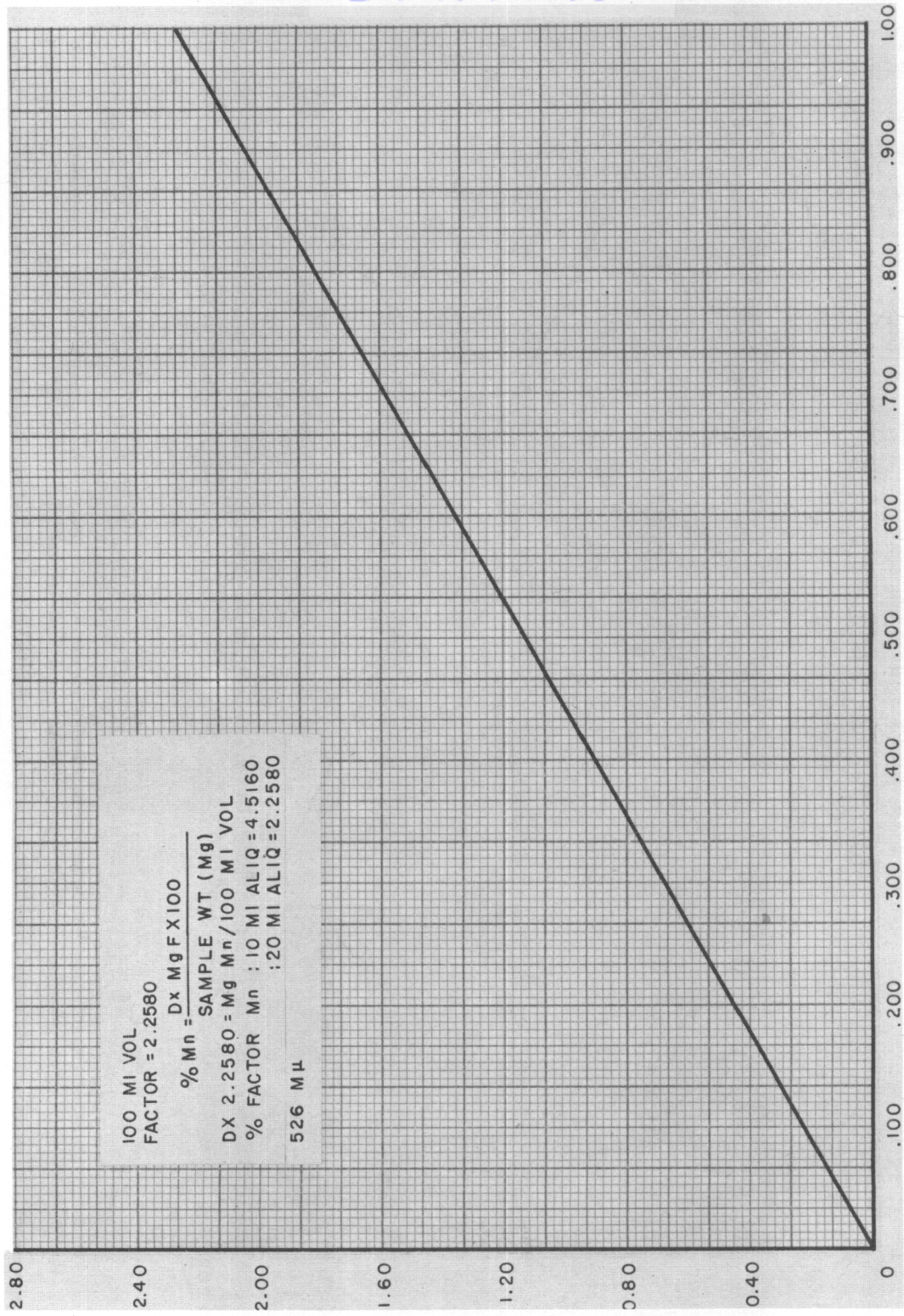

Figure 9. Manganese Calibration Curve (Aluminum Alloy)

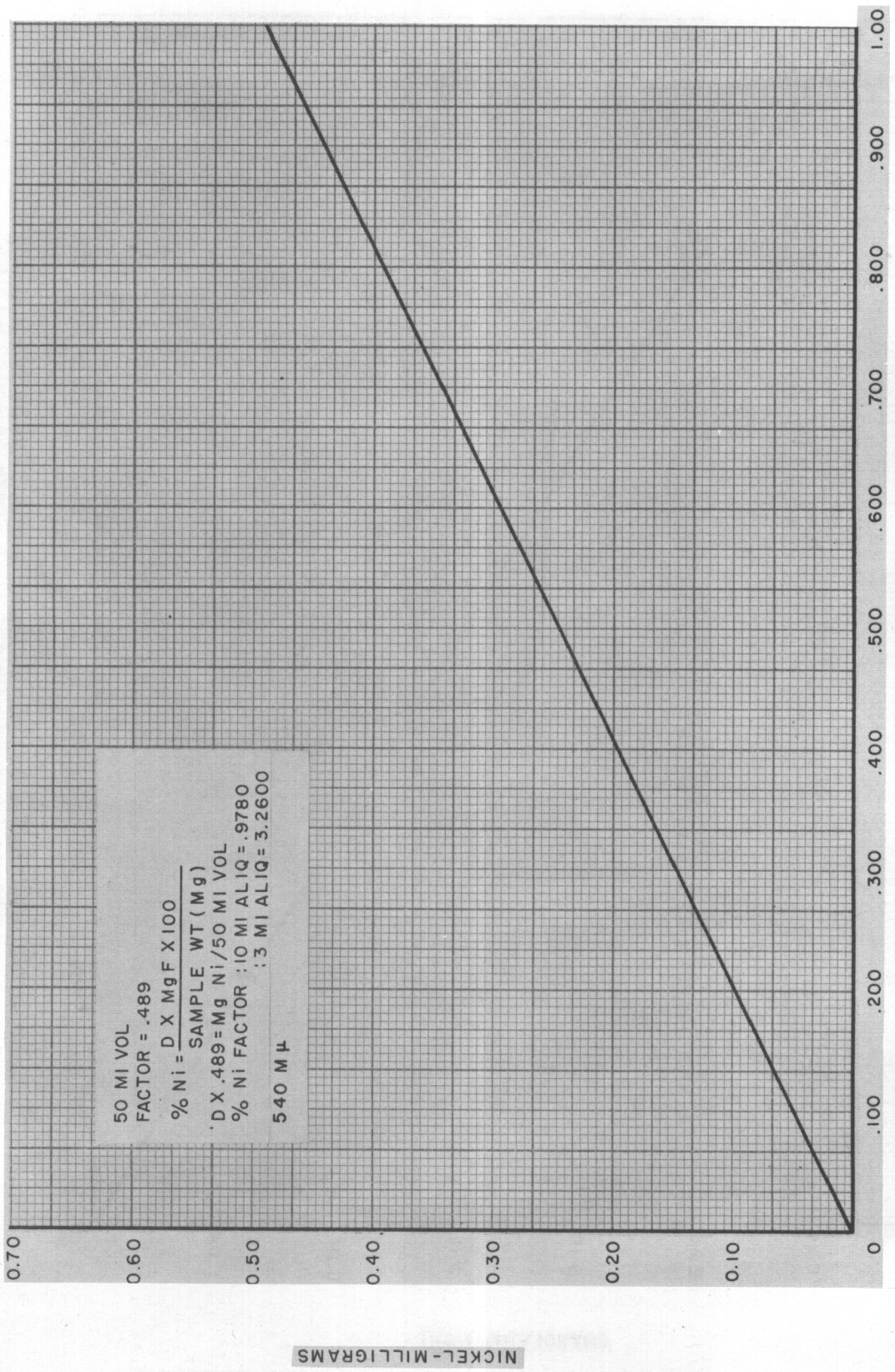

Figure 10. Nickel Calibration Curve (Aluminum Alloy)

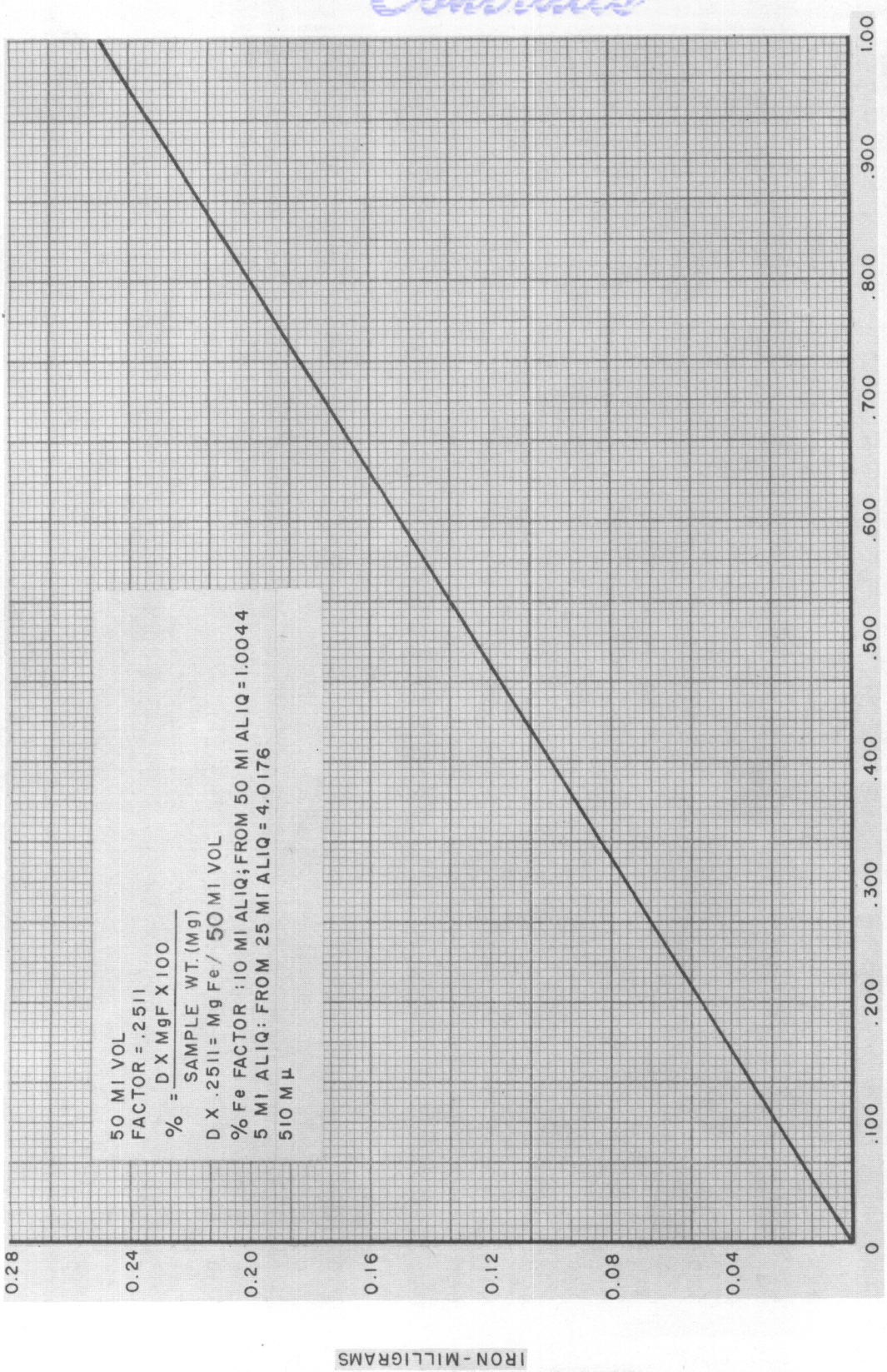

Figure 11. Iron Calibration Curve (Aluminum Alloy)

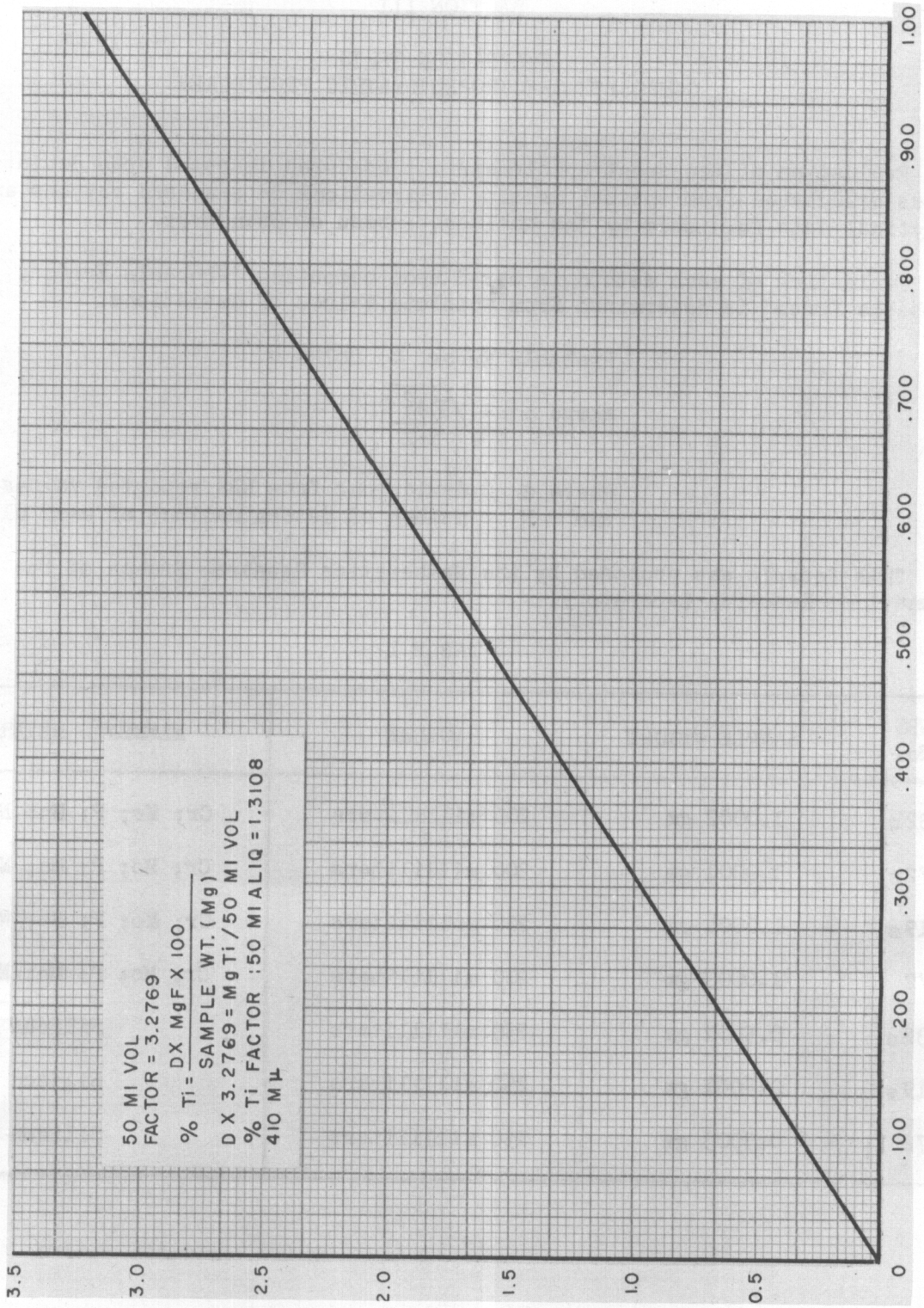

Figure 12. Titanium Calibration Curve (Aluminum Alloy)

SECTION III

EVALUATION TESTS
COMPOSITE SPECTROPHOTOMETRIC PROCEDURES

Evaluation of the spectrophotometric procedures is based upon deviation values calculated from optical density observations on standard samples and analytical data furnished by the National Bureau of Standards.

Evaluation of each method is based upon computing "Probable Error". "Probable Error" is determined from absolute values of deviations.

$$\text{Probable Error} = .6745\,\sigma$$

$$\text{where } \sigma = \sqrt{\frac{\Sigma d^2}{N-1}}$$

where d = deviations from NBS reported values
and N = number of determinations of each element

This formula was proposed by the Mathematics Research Branch of the Aeronautics Research Laboratory.

TABLE 1

NBS No.	SAMPLE WEIGHT	VOLUME	ELEMENTS DETERMINED
32c	1.0002 gm	200 milliliters	Cr; Mo; P; Mn; Ni; Cu
72b	1.0001 gm	200 milliliters	Cr; Mo; P; Mn; Ni; Cu
19e	1.0004 gm	200 milliliters	Cr; Mo; P; Mn; Ni; Cu
72	1.0003 gm	200 milliliters	Cr; Mo; P; Mn; Ni; Cu
32c	0.5002 gm	250 milliliters	Silicon
19e	0.5001 gm	250 milliliters	Silicon
72	0.5003 gm	250 milliliters	Silicon

TABLE 2

EVALUATION TEST—PHOSPHORUS

NBS No.	ALIQUOTS	OPTICAL DENSITY	FACTOR	SAMPLE % P	STANDARD % P	DEVIATION
32c	20 milliliters	0.210 0.205	0.0513	0.011 0.011	0.010	+0.001 +0.001
72b	20 milliliters	0.200 0.195	0.0513	0.010 0.010	0.009	+0.001 +0.001
19e	20 milliliters	0.695 0.685	0.0513	0.036 0.035	0.033	+0.003 +0.002
72	20 milliliters	0.310 0.300	0.0513	0.016 0.015	0.016	0.000 -0.001
Probable Error = 0.001						

TABLE 3

EVALUATION TEST—CHROMIUM

NBS No.	ALIQUOTS	OPTICAL DENSITY	FACTOR	SAMPLE % Cr	STANDARD % Cr	DEVIATION
32c	20 milliliters	0.640 0.645	1.0164	0.650 0.656	0.654	-0.004 +0.002
72b	20 milliliters	0.935 0.940	1.0164	0.950 0.955	0.962	-0.012 -0.007
19e	20 milliliters	0.035 0.040	1.0164	0.036 0.041	0.038	-0.002 +0.003
72	20 milliliters	0.895 0.900	1.0164	0.910 0.915	0.911	-0.001 +0.004
Probable Error = 0.004						

TABLE 4

EVALUATION TEST—MOLYBDENUM

NBS No.	ALIQUOTS	OPTICAL DENSITY	FACTOR	SAMPLE % Mo	STANDARD % Mo	DEVIATION
32 c	5 milliliters	0.123 0.120	0.5276	0.065 0.063	0.063	+0.002 0.000
72 b	5 milliliters	0.421 0.419	0.5276	0.222 0.221	0.223	—0.001 —0.002
19 e	5 milliliters	0.025 0.023	0.5276	0.013 0.012	0.012	+0.001 0.000
72	5 milliliters	0.280 0.283	0.5276	0.148 0.149	0.149	—0.001 0.000
Probable Error = 0.001						

TABLE 5

EVALUATION TEST—MANGANESE

NBS No.	ALIQUOTS	OPTICAL DENSITY	FACTOR	SAMPLE % Mn	STANDARD % Mn	DEVIATION
32 c	20 milliliters	0.335 0.330	2.2580	0.756 0.745	0.752	+0.004 —0.007
72 b	20 milliliters	0.225 0.230	2.2580	0.508 0.519	0.520	—0.012 —0.001
19 e	20 milliliters	0.220 0.217	2.2580	0.497 0.490	0.491	+0.006 —0.001
Probable Error = 0.005						

TABLE 6

EVALUATION TEST—NICKEL

NBS No.	ALIQUOTS	OPTICAL DENSITY	FACTOR	SAMPLE % Ni	STANDARD % Ni	DEVIATION
32 c	3 milliliters	0.375 0.370	3.2600	1.22 1.21	1.20	+0.002 +0.001
72 b	10 milliliters	0.120 0.125	0.9780	1.17 1.22	1.13	+0.004 +0.009
19 e	10 milliliters	0.100 0.104	0.9780	0.098 0.102	0.093	+0.005 +0.009
72	10 milliliters	0.300 0.305	0.9780	0.293 0.298	2.88	+0.005 +0.010
Probable Error = 0.005						

TABLE 7

EVALUATION TEST—COPPER

NBS No.	ALIQUOTS	OPTICAL DENSITY	FACTOR	SAMPLE % Cu	STANDARD % Cu	DEVIATION
32 c	20 milliliters	0.090 0.095	1.0455	0.094 0.099	0.099	-0.005 0.000
72 b	20 milliliters	0.090 0.095	1.0455	0.094 0.099	0.098	-0.004 +0.001
19 e	20 milliliters	0.160 0.155	1.0455	0.167 0.162	0.166	+0.001 -0.004
72	20 milliliters	0.065 0.060	1.0455	0.068 0.063	0.064	+0.004 -0.001
Probable Error = 0.002						

TABLE 8

EVALUATION TEST—SILICON

NBS No.	ALIQUOTS	OPTICAL DENSITY	FACTOR	SAMPLE % Si	STANDARD % Si	DEVIATION
32 c	25 milliliters	0.492 0.495	0.5670	0.279 0.281	0.281	-0.002 0.000
72 b						
19 e	25 milliliters	0.300 0.305	0.5670	0.170 0.176	0.173	-0.003 +0.003
72	25 milliliters	0.240 0.245	0.5670	0.136 0.139	0.137	-0.001 +0.002
Probable Error = 0.002						

SECTION IV

CONCLUSIONS

Spectrophotometric analysis for constituents in low alloys of steel and alloys of aluminum give the same results as those obtained by conventional gravimetric and volumetric methods, but the time is less than 50 percent of that required for the conventional gravimetric or volumetric methods.

Therefore, these procedures definitely establish methods which will result in the saving of man-hours in the analysis of low-alloy steels and alloys of aluminum used in aircraft.

This report outlines steps and techniques that can be performed by semi-skilled analysts.