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SPECTROPHOTOMETRIC-CUPRETHOL METHOD FOR THE QUANTITATIVE DETERMINATION OF COPPER IN AVIATION FUELS

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FOREWORD

This report was prepared by the Lubricants Section, Organic Materials Branch, Materials Laboratory, Directorate of Research, Wright Air Development Center, where the work was performed. This work, conducted by O. M. Ballentine, is part of an investigation into the effects of small quantities of copper on the stability of aircraft engine fuel as authorized by Project 3048 "Aviation Fuels"; Task No. 73300 "Fuel Additives for Storage Stability" (formerly RDO 613-12 "Aircraft Fuels").

ABSTRACT

A method has been established by this Center for the quantitative determination of ionic copper in aviation fuels in concentrations as low as 1 ppm of copper. In this method the cupric ion reacts with a compound prepared from carbon disulfide and diethanolamine to form the yellow salt complex of bis(2-hydroxyethyl)dithiocarbamic acid. The concentration of copper is determined by first measuring the optical density of the resulting solution, at the maximum wave length, with an absorption spectrophotometer and then relating this optical measurement to a previously prepared concentration optical density curve.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

M. R. WHITMORE
Technical Director
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I. DISCUSSION ON THE SPECTROPHOTOMETRIC-CUPRETHOL METHOD FOR THE QUANTITATIVE COPPER DETERMINATION IN AVIATION FUELS

A method for the quantitative determination of ionic copper in aviation fuels in concentrations as low as 1 ppm of copper has been established.

In this method, the cupric ion reacts with a reagent prepared from carbon disulfide and diethanolamine to form the yellow salt complex of bis (2-hydroxyethyl) dithiocarbamic acid. This compound is water soluble and does not necessitate the use of any agents required for colloidal suspension stabilization nor the use of solvents to extract insoluble salts. The copper content is determined by measuring the optical density of the salt solution, at the maximum wave length, with an absorption spectrophotometer. The concentration of copper can then be obtained from a previously calibrated curve relating concentration of copper to optical densities.

If the specific extinction coefficient is known (this value can be determined experimentally by measuring the extinction of a standard copper solution), it is possible to obtain the copper concentration directly by using Beer-Lamberts law, i.e. $E = kcl$ where E values are measured optical densities (or extinctions); k is the specific extinction coefficient; c is the concentration (grams/liter); and l is the depth of the absorption cells in centimeters.

It is desirable in these studies to remove iron from the fuel samples since this element will also form a complex salt with the precipitating agent and consequently mask the true color change. The interference of ferric salts may be eliminated by removing the iron as a hydroxide. Other metallic elements, sulfur, chlorine and phosphorus, will not usually interfere in the copper determinations, unless they are present in unusually large concentrations.

An outline of the quantitative determination of the copper is given. This method is separated into the following headings:

A. Equipment
B. Reagents Employed
C. Preparation of Calibration Curve
D. Experimental Procedure
E. Calculation of Copper Concentration

For reference purposes, a typical calibration curve relating milligrams of copper to optical density is furnished in Figure 1. The optical densities were determined on a Beckman Model DU Photoelectric Quartz Spectrophotometer and are given in Table I.

Various samples of aviation fuels, which were aged at 130°F for a period of a year in the presence of metallic copper, were used in this experiment to determine the concentration of copper being absorbed in the fuels under these conditions. The concentration of copper in these samples was determined in duplicate to determine the repeatability of the method described in this report. These data are given in Table II.

The accuracy of this method is relative to the accuracy of quantitative copper determinations made for establishing a copper content-optical density curve. It is assumed that the entire amount of an accurately weighed copper sample reacts with the cuprethol reagent to form the colored solution for optical measurements. Since the reaction is conducted under such favorable equilibrium conditions to force the reaction to the formation of the copper complex (e.g. using an excess of cuprethol reagent) then, theoretically, a complete reaction is expected. The accuracy of copper determination in fuels will vary with the composition of such fuels since, as previously mentioned, some elements will interfere and possibly mask the desired reaction of the cupric ion and substituted carbamic acid. If extreme accuracies are desired, it may be necessary to obtain a sample of copper-free fuel from the same crude oil or geographical vicinity as the one containing copper so that the variable of interfering substances can be eliminated. This is accomplished by using the copper-free fuel as a blank.

II. SPECTROPHOTOMETRIC-CUPRETHOL METHOD FOR THE QUANTITATIVE DETERMINATION OF COPPER IN AVIATION FUELS

A. Equipment

Beckman Photoelectric Quartz Spectrophotometer equipped with a color filter of 450 mμ and light absorption cells 1.0 cm in thickness.

B. Reagents Employed

1. Ammonium Hydroxide, concentrated, cp.
2. Congo Red Indicator Paper
3. Cuprethol Reagent

Solution A: Dissolve 4.0 g. of diethanolamine in 200 ml of methanol.

Solution B: Dissolve 1.00 ml of carbon disulfide in 200 ml of methanol. Combining solutions A and B in equal volumes will give the cuprethol reagent, diethanolammonium bis (2-hydroxyethyl) dithiocarbamate. The cuprethol reagent should be discarded after one day's use.

4. Ferric Chloride Solution

Dissolve 16.5 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in water containing 1 ml of concentrated Hydrochloric Acid. Dilute to 1 liter.

5. Hydrochloric Acid 1:9

6. Sodium Acetate Solution

Dissolve 200 g of sodium acetate trihydrate ($NaC_2H_3O_2 \cdot 3H_2O$) in water and dilute to 1 liter.

7. Sodium Pyrophosphate Solution

Dissolve 200 g of sodium pyrophosphate decahydrate ($Na_4P_2O_7 \cdot 10H_2O$) in water and dilute to 1 liter.

8. Standard Copper Solution

Dissolve 0.2000 g of pure copper metal (99.9% copper) in 10 ml of 1:1 nitric acid, add 2 ml of concentrated sulfuric acid and evaporate to complete dryness. Dissolve the residue in water and dilute to 1 liter. Dilute 10 ml of this solution to 100 ml to obtain a solution containing 0.020 mg of copper/ml.

C. Preparation of Calibration Curve

Introduce exactly 0, 2, 4, 6, 8, and 10 ml of standard copper solution (0.020 mg copper/liter) into separate 100 ml volumetric flasks. Dilute to approximately 50 ml with water, and add 2 ml of 1:9 hydrochloric acid and 10 ml of sodium acetate solution. Add 1 ml of cuprethol reagent and dilute to the 100 - ml mark. Mix thoroughly and determine within 10 to 60 minutes the optical density relative to distilled water by using an absorption spectrophotometer. The corrected optical density is obtained by subtracting the "blank" sample (containing 0 ml of standard copper solution) from each optical density. A calibration curve can then be prepared by plotting the corrected optical densities vs mg of copper/100 ml.

D. Experimental Procedure

1. Transfer 15.0 ml [1] of a thoroughly shaken sample of fuel by a volumetric pipette, to a 90 mm porcelain evaporating dish. [2]

2. Ignite the fuel sample and allow the sample to burn under an exhaust hood until only carbon and ash remain. Completely oxidize the carbon by either ignition over a Fischer burner or by placing the evaporating dish and its contents in a kiln. Heat slowly to avoid loss by splattering.

3. Add 5 ml of concentrated hydrochloric acid, cover the dish and digest at a low temperature until all ash is completely dissolved.

4. Filter the acid solution through ashless filter paper. If any residue remains in the evaporating dish add an additional 5 ml of concentrated hydrochloric acid, digest, filter, and combine with the first acid filtrate.

5. Transfer the acid mixture to a 125 ml erlenmeyer flask.

6. Add 2 ml of concentrated hydrochloric acid and 3 ml of ferric chloride solution. Dilute the solution to approximately 25 ml.

7. Drop a small piece of congo red indicator paper in the solution. Neutralize the solution with concentrated ammonium hydroxide and add 1 to 2 ml in excess.

8. Heat the solution to boiling and place immediately on a steam bath. The solution should be allowed to digest until all the iron has been removed as the hydroxide (observed as a reddish brown precipitate). Approximately 30 minutes will be required for this digestion.

9. Filter, while hot, through a Whatman No. 41 (fast flowing) filter paper into a 100 ml volumetric flask. Wash the precipitate several times with boiling water.

10. Allow the filtrate to cool to room temperature and dilute the solution to approximately 50 ml.

11. Drop a small piece of congo red indicator paper in the solution and add 1:9 hydrochloric acid dropwise until the indicator paper just changes to blue. Add exactly 2 ml in excess.

12. Add 10 ml of sodium acetate to produce a pH of approximately 5.0. Mix thoroughly.

13. Add 1 ml of cuprethol reagent and dilute to the 100 - ml mark. Mix thoroughly and determine the corrected optical density as discussed in the Preparation of the Calibration Curve.

14. Make a blank determination following the same procedure omitting only the fuel sample. The blank will be used in obtaining the corrected optical density.

E. Calculation of Copper Concentration

1. The concentration of copper is obtained from the calibration curve by converting the corrected optical density (subtracting the optical density of the blank from that of the sample) into milligrams of copper/ 100 ml.

2. The per cent of copper can then be calculated by the following working equation: *

$$\text{Copper, per cent} = \frac{5S}{AW} \times 100$$

Note$_1$ To determine the percentage of copper per weight of sample, calculate this weight through density measurements.

Note$_2$ Ignition vessels, especially new porcelain, should be treated by adding an alcoholic solution of sodium acetate. The treated vessels should then be heated in a kiln followed by a 1:1 hydrochloric acid wash.

* To determine the percentage of copper per weight of sample, calculate this weight through density measurements.

Where

S = milligrams of copper corresponding to the corrected optical density

A = volume of aliquot obtained after dry ashing (ml)

W = weight of sample, fuel (g)

III BIBLIOGRAPHY

Articles

1. Shell Development Company, Analytical Department

   Determination of Copper in Acqueous Solutions

2. Industrial Engineering Chemistry, Analytical Ed., 3, 314, (1931).

3. Conn. and co-workers, Industrial Engineering Chemistry, Analytical Ed., 7, 15, (1935).

4. ASTM Standards on Petroleum Products and Lubricants, 1951

   Test for Copper in New and Used Lubricating Oils

Books

1. N. H. Furman

   Scotts Standard Method of Chemical Analysis

2. N. V. Sidgwick

   The Chemical Elements and Their Compounds

   Complexes of Copper

TABLE I

Optical Densities for Solutions Containing Known Concentrations of Copper to Obtain a Calibration Curve (Figure 1)

Copper Content mg/dl	Observed Optical Density	True Optical Density
0.00	0.011	0.011
0.04	0.086	0.075
0.08	0.157	0.146
0.12	0.228	0.217
0.16	0.305	0.294
0.20	0.367	0.356

TABLE II

Concentrations of Copper in Aviation Fuels
Showing Repeatability of the Absorption Spectrophotometric-
Cuprethol Method

Aviation Fuel	Run	Concentration of Copper (mg/dl)	Deviation of each Run from the Mean
1	1	0.005	0.001
	2	0.004	
2	1	0.007	0.000
	2	0.008	
3	1	0.000	0.000
	2	0.000	
4	1	0.000	0.004
	2	0.007	
5	1	0.000	0.000
	2	0.000	
6	1	0.050	0.001
	2	0.052	
7	1	0.010	0.003
	2	0.005	
8	1	0.007	0.000
	2	0.007	
9	1	0.010	0.003
	2	0.015	

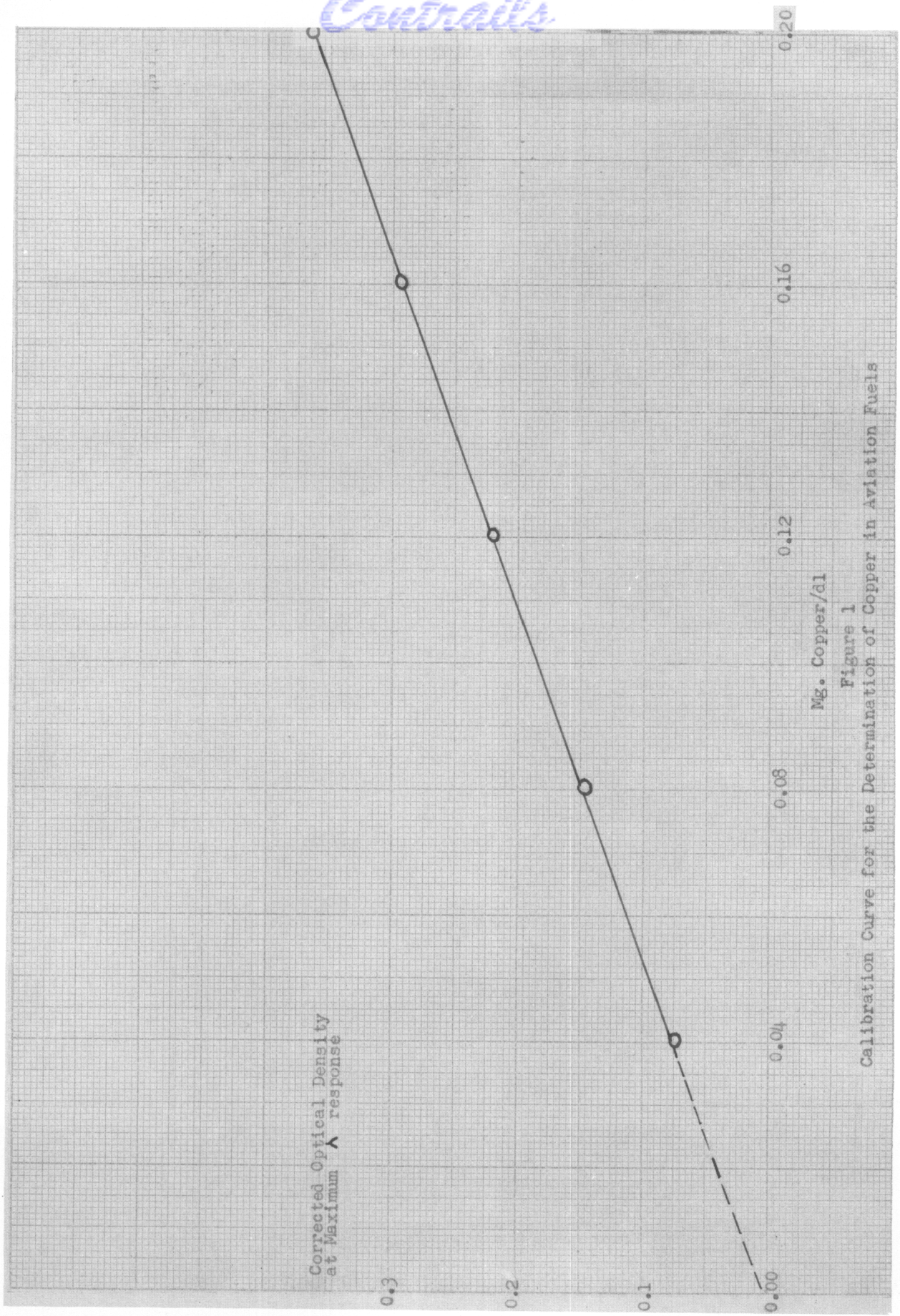

Figure 1
Calibration Curve for the Determination of Copper in Aviation Fuels