



Designation: **D 6732 – 04₂**

An American National Standard

Standard Test Method for Determination of Copper in Jet Fuels by Graphite Furnace Atomic Absorption Spectrometry¹

This standard is issued under the fixed designation D 6732; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope*

1.1 This test method covers the determination of copper in jet fuels in the range of 5 to 100 $\mu\text{g}/\text{kg}$ using graphite furnace atomic absorption spectrometry. Copper contents above 100 $\mu\text{g}/\text{kg}$ may be determined by sample dilution with kerosene to bring the copper level into the aforementioned method range. When sample dilution is used, the precision statements do not apply.

NOTE 1—This test method is not intended for use in specifications.

1.2 The values stated in SI units are to be regarded as standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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*A Summary of Changes section appears at the end of this standard.

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products²

D 4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination²

D 6299 Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance³

3. Terminology

3.1 Definitions:

3.1.1 *radiant power, P, n*—the rate at which energy is transported in a beam of radiant energy.

3.1.2 *transmittance, T, n*—the ratio of the radiant power transmitted by a material to the radiant power incident upon it.

3.2 Definitions of Terms Specific to This Standard:

3.2.1 *absorbance, A, n*—the logarithm to the base 10 of the ratio of the reciprocal of the transmittance, T:

$$A = \log_{10}(1/T) = -\log_{10}T \quad (1)$$

3.2.2 *integrated absorbance, A_i, n*—the integrated area under the absorbance peak generated by the atomic absorption spectrometer.

4. Summary of Test Method

~~4.1 An aliquot (typically 10 µL) of the sample is pipetted onto a platform in the~~

4.1 The graphite furnace. The furnace is aligned in the light path of the atomic absorption spectrometer equipped with background correction. An aliquot (typically 10 µL) of the sample is pipetted onto a platform in the furnace. The furnace is heated to low temperature to dry the sample completely without spattering. The furnace is then heated to a moderate temperature to eliminate excess sample matrix. The furnace is further heated very rapidly to a temperature high enough to volatilize the analyte of interest. It is during this step that the amount of light absorbed by the copper atoms is measured by the spectrometer.

4.2 The light absorbed is measured over a specified period. The integrated absorbance *A_i* produced by the copper in the samples is compared to a calibration curve constructed from measured *A_i* values for organo-metallic standards.

5. Significance and Use

5.1 At high temperatures aviation turbine fuels can oxidize and produce insoluble deposits that are detrimental to aircraft propulsion systems. Very low copper concentrations (in excess of 50 µg/kg) can significantly accelerate this thermal instability of aviation turbine fuel. Naval shipboard aviation fuel delivery systems contain copper-nickel piping, which can increase copper levels in the fuel. This test method may be used for quality checks of copper levels in aviation fuel samples taken on shipboard, in refineries, and at fuel storage depots.

6. Interferences

6.1 Interferences most commonly occur due to light that is absorbed by species other than the atomic species of interest. Generally, this is due to undissociated molecular particles from the sample matrix. The char step in the furnace program is used to eliminate as much of the matrix as possible before the atomization step. Spectrometers are equipped with background correction capabilities to control further possibilities of erroneous results due to molecular absorption.

7. Apparatus

7.1 *Atomic Absorption Spectrometer*—An atomic absorption spectrometer with the capability of setting the wavelength at 324.8 nm, setting the slit width at typically 0.7 nm, and using peak area integration for the atomic and background readings shall be used. The spectrometer shall be equipped with the following:

7.1.1 *Copper Hollow Cathode Lamp*—as the elemental light source.

7.1.2 *Background Correction Capability*—to cover the 324.8 nm wavelength range.

7.1.3 *Graphite Furnace Accessory Atomizer*—which uses pyrolytically coated graphite tubes with L'vov platforms.

7.2 *Autosampler or Manual Pipettor*—capable of reproducibly delivering 10 ± 0.5 µL aliquots of samples, standards, and blank to the graphite furnace.

7.3 *Analytical Balance*—capable of weighing $100 \text{ g} \pm 0.0001 \text{ g}$.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such

² Annual Book of ASTM Standards, Vol 05.02.

³ Annual Book of ASTM Standards, Vol 05.04.

specifications are available.⁴ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

8.2 *Odorless or Low Odor Kerosene*, filtered through silica gel.

8.3 *100 mg/kg Organo-metallic Standard for Copper*, or a multielement standard containing copper at 100 mg/kg.

8.4 *Silica Gel*, 100 to 200 mesh.

8.5 *Argon Gas, 99.999%*, (**Warning**—Argon is a compressed gas under high pressure) for graphite furnace gas flow system.

8.6 *Quality Control (QC) Samples*, preferably are portions of one or more kerosene materials that are stable and representative of the samples of interest. These QC samples can be used to check the validity of the testing process as described in Section 14. Use a stable QC concentrate, and dilute it on the day of the QC check to the trace level required.

9. Sampling

9.1 Samples shall be taken in accordance with procedures described in Practice D 4057.

9.2 Samples shall be thoroughly mixed in their containers immediately prior to testing.

10. Calibration and Standardization

10.1 *Preparation of Standards:*

10.1.1 *Nominal 1 mg/kg Intermediate Stock Standard*—Accurately weigh a nominal 0.50 g (All masses are measured to the nearest 0.0001 g.) of the 100 mg/kg stock organo-metallic standard into a suitable container (capable of being sealed for mixing). Suitable sample containers are described in Practice D 4306. Add enough odorless kerosene to bring the total mass to a nominal 50.00 g. Seal the container and mix well. See 12.1.1 for calculation of actual concentration.

10.1.2 *Working Standards of Nominally 20, 40, 60, 80, and 100 µg/kg*—Accurately weigh a nominal (All masses are measured to the nearest 0.0001 g.) 0.20, 0.40, 0.60, 0.80, and 1.00 g of the nominal 1 mg/kg intermediate stock standard into five suitable containers. Add enough odorless kerosene to each container to bring the total mass to a nominal 10.00 g. Seal containers and mix well. This produces working standards of nominal 20, 40, 60, 80, and 100 µg/kg, respectively. See 12.1.2 for calculations of actual concentrations.

10.2 *Calibration:*

10.2.1 Prepare a standard calibration curve by using the odorless kerosene as a blank and each of the five working standards. The instrument measures the integrated absorbance A_i of 10 µL of each working standard and blank. The intermediate stock standard and working standards shall be prepared daily.

10.2.2 The calibration curve is constructed by plotting the corrected integrated absorbances (on y-axis) versus the concentrations of copper in the working standards in µg/kg (on x-axis). See 12.2.1 for calculating corrected integrated absorbance. Fig. 1 shows a typical calibration curve for atomic absorption spectroscopy. Many atomic absorption spectrometers have the capability of constructing the calibration curve internally or by way of computer software. Construct the best possible fit of the data with available means.

11. Procedure

11.1 Set the spectrometer at a wavelength of 324.8 nm and a slit width of typically 0.7 nm. Align the hollow cathode lamp and

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

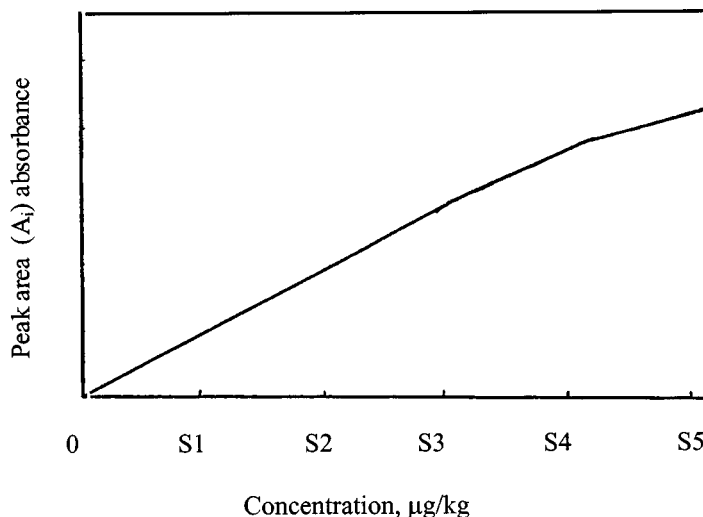


FIG. 1 Typical Calibration Curve of Copper Concentration versus Integrated Absorbance (A_i)

furnace assembly to obtain maximum transmittance.

11.2 Condition new (or reinstalled) graphite tube and L'vov platform with the temperature program provided by the spectrometer manufacturer until the baseline shows no peaks.

11.3 Calibrate the graphite furnace temperature controller at 2300°C according to the spectrometer manufacturer's instructions.

11.4 When an autosampler is used with the graphite furnace, use odorless kerosene as the rinse solution. Use only autosampler cups made of polyethylene, polypropylene, or TFE-fluorocarbon. Do not use polystyrene cups as these degrade and leak when used with organic solvents.

11.5 Calibrate the instrument by pipetting a 10 µL aliquot of odorless kerosene as a blank and then 10 µL of each of the standards onto the platform in the graphite tube. Then pipette 10 µL of each sample into the furnace and carry each through the furnace program. Run each blank, standard, and sample through the furnace program listed in Table 1. Compare the integrated absorbance of each sample to the corrected calibration curve generated from the blank and standards to determine the copper concentration of each. Run each sample in duplicate.

NOTE 12—Aliquots other than 10 µL may be pipetted into the furnace. Volumes from 5 to 40 µL may be used, as long as the volume used is consistent between blanks, standards, and samples. If this is done, dry temperatures, char temperature, ramp times, and/or hold times, or a combination thereof, may need to be adjusted.

12. Calculations

12.1 Standard Concentrations:

12.1.1 Calculate the copper concentration of the nominal 1 mg/kg intermediate stock standard as follows:

$$c_i = c_s m_s / m_t \quad (2)$$

where:

c_i = copper concentration of the intermediate stock standard, mg/kg,

c_s = copper concentration of the certified (nominal 100 mg/kg) organo-metallic standard, mg/kg,

m_s = measured mass of certified organo-metallic standard, g, and

m_t = measured mass of solution of organo-metallic standard and kerosene diluent, g.

12.1.2 Calculate the copper concentrations of the working standards (nominal 20, 40, 60, 80, and 100 µg/kg) as follows:

$$c_w = 1000 c_i m_i / m_f \quad (3)$$

where:

c_w = copper concentration of a working standard, µg/kg,

c_i = copper concentration of the (nominal 1 mg/kg) intermediate stock standard, mg/kg,

m_i = measured mass of the intermediate stock standard, g, and

m_f = measured mass of solution of intermediate stock standard and kerosene diluent, g.

12.2 Standard Calibration Curve Correction and Fuel Copper Determination:

12.2.1 Correct the standard calibration curve for any copper present in the kerosene blank and diluent by subtracting the kerosene blank integrated absorbance A_o from each of the integrated absorbances of the working standards, A_w :

$$\text{corrected integrated absorbance} = A_w - A_o \quad (4)$$

12.2.2 Plot the corrected integrated absorbance values for the working standards versus their concentrations to provide the corrected standard calibration curve. The fuel sample concentration is determined from its integrated absorbance value and the corrected standard calibration curve.

13. Report

13.1 Report the average value of the two runs, rounded to the nearest 1 µg/kg.

14. Quality Control

14.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample (see 8.6). Fig.

TABLE 1 Typical Graphite Furnace Operational Parameters

Step	Dry 1 ^A	Dry 2 ^A	Char ^B	Atomize ^C	Clean	Cool
Temp, °C	100	150	800	2300	2600	20
Ramp, s	10	10	15	0	1	1
Hold, s	15	20	35	5	5	10
Gas Flow, mL/min	300	300	300	0	300	300
Read				ON		

^A The dry temperatures, ramp times, and hold times shall be optimized so that the sample dries completely, without boiling and spattering.

^B The ramp time for the char step may be lengthened if it appears that an excess amount of smoke from the sample matrix is generated very quickly as the furnace heats from Dry 2 to char. Also, all of the smoke shall be evolved at least 5 s before the end of the char cycle. If smoke still evolves at the end of the char cycle, the hold time shall be lengthened.

^C For the spectrometer trace of absorbance versus atomization hold time, the absorbance at the end of the atomization hold time should return to the initial baseline absorbance. If this is not observed, increase the atomization hold time until this is attained.

2 illustrates the problem of trace level copper migration to sample container walls at ambient temperature which depletes trace organo-copper QC samples with time. Storage in a refrigerated environment (5°C) minimizes the migration of trace level copper.

14.1.1 When QC / Quality Assurance (QA) protocols are already established in the testing facility, these may be used when they confirm the reliability of the test result.

14.1.2 When there is no QC / QA protocol established in the testing facility, Appendix X1 can be used as the QC / QA system.

15. Precision and Bias ⁵

15.1 *Precision*—The precision of this test method (illustrated in Fig. 3) as determined by the statistical examination of the interlaboratory test results is as follows:

15.1.1 *Repeatability*—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the following values only one case in twenty:

$$\text{Repeatability} = (X + 1)^{0.5} \tag{5}$$

where:

X = the average of two results in µg/kg.

15.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would in the long run, exceed the following values only in one case in twenty:

$$\text{Reproducibility} = 4.5 (X + 1)^{0.5} \tag{6}$$

where:

X = the average of two results in µg/kg.

⁵ Supporting data are available from have been filed at ASTM International Headquarters in the form of a research report. Request RR:D02-1512, and may be obtained by requesting Research Report RR: D02-1512.

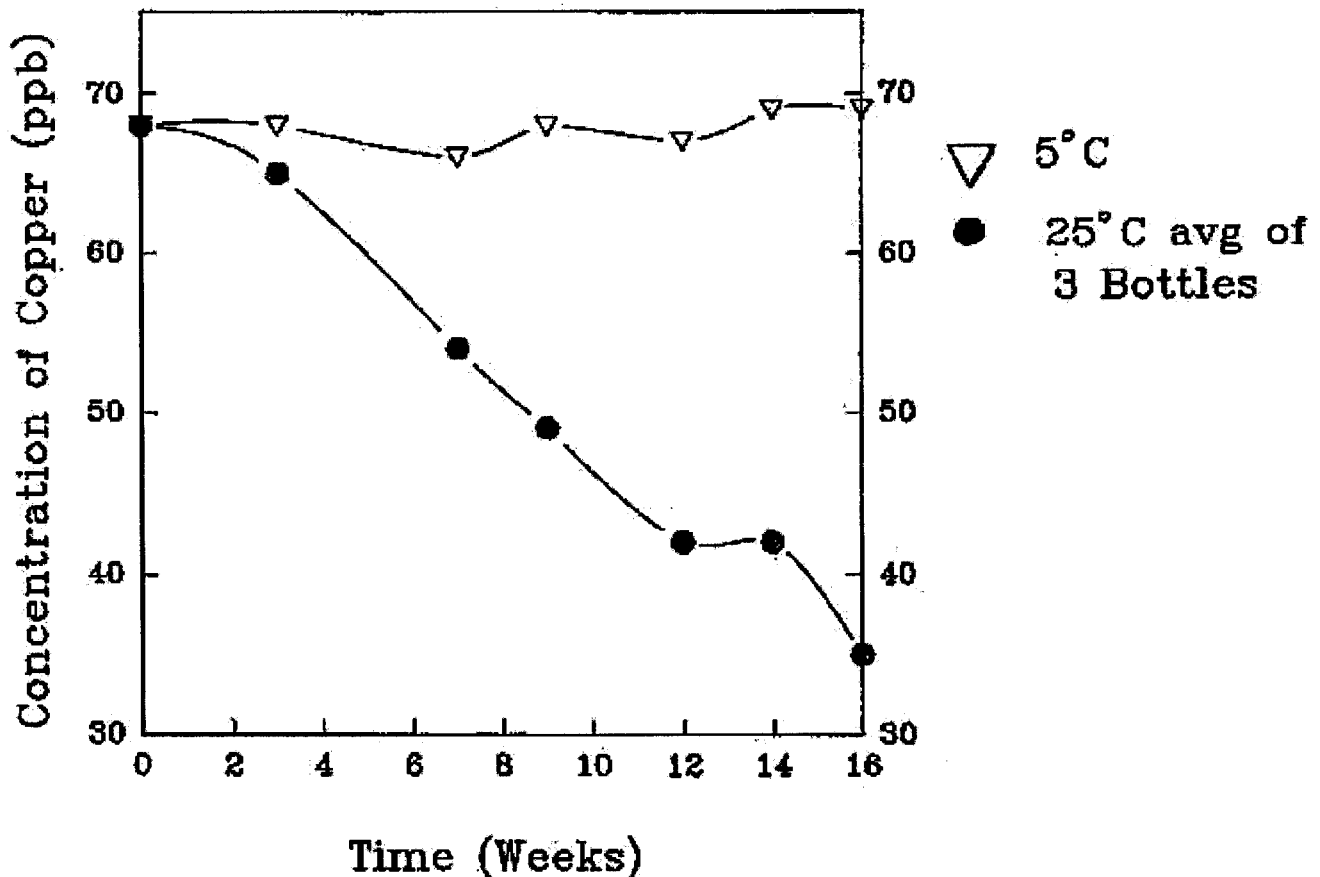


FIG. 2 Time Study of Trace Copper in Kerosene Contained in Teflon Bottles

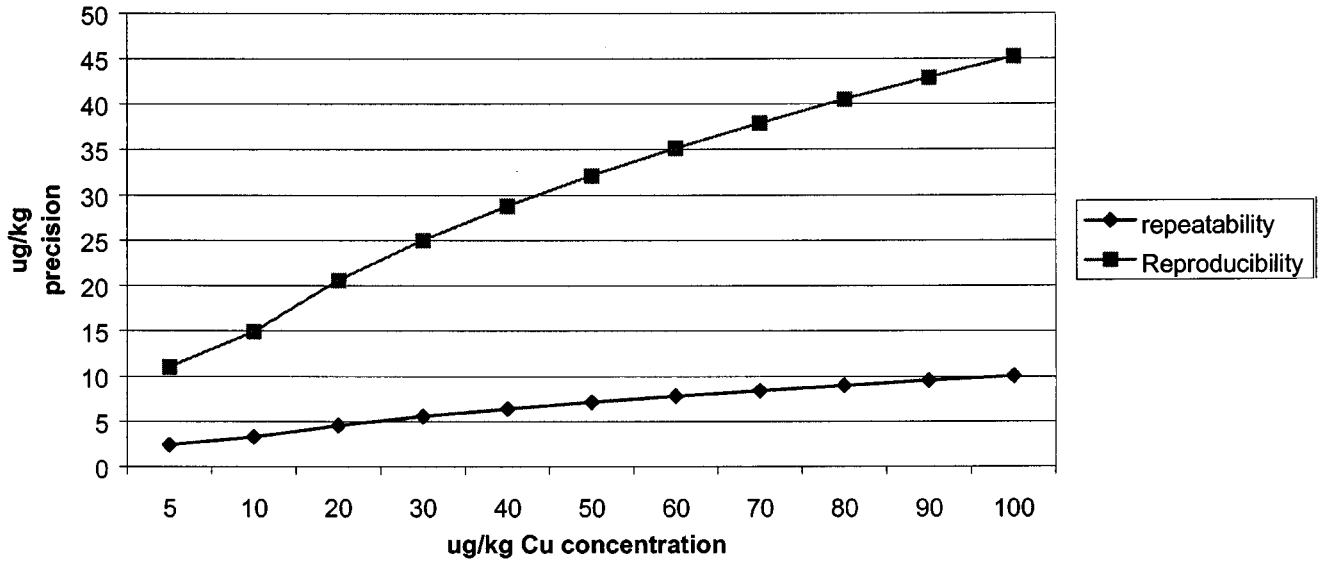


FIG. 3 Precision for the Determination of Copper in Jet Fuels by Graphite Furnace Atomic Absorption

15.2 *Bias*—Since there is no accepted reference material for determining bias for this test method, no statement on bias is being made.

16. Keywords

- 16.1 absorbance units; atomic absorption spectrometer; aviation fuel; copper; graphite furnace; jet fuel; spectrometer

APPENDIX

(Nonmandatory Information)

X1. QUALITY CONTROL

X1.1 Confirm the performance of the instrument or the test procedure by analyzing a quality control (QC) sample.

X1.2 Prior to monitoring the measurement process, the user of the test method needs to determine the average value and control limits of the QC sample. See Practice D 6299 and MNL 7.⁶

X1.3 Record the QC results and analyze by control charts or other statistically equivalent techniques to ascertain the statistical control status of the total testing process. See Practice D 6299 and MNL 7.⁶ Any out-of-control data should trigger investigation for root cause(s). The results of this investigation may, but not necessarily, result in instrument re-calibration.

X1.4 In the absence of explicit requirements given in the test method, the frequency of QC testing is dependent on the criticality of the quality being measured, the demonstrated stability of the testing process, and customer requirements. Generally, a QC sample is analyzed each testing day with routine samples. The QC frequency should be increased if a large number of samples are routinely analyzed. However, when it is demonstrated that the testing is under statistical control, the QC testing frequency may be reduced. The QC sample precision should be checked against the ASTM test method precision to ensure data quality.

X1.5 It is recommended that, if possible, the type of QC sample that is regularly tested be representative of the material routinely analyzed. An ample supply of QC sample material should be available for the intended period of use, and must be homogenous and stable under the anticipated storage conditions. See Practice D 6299 and MNL 7,⁶ or a combination thereof, for further guidance on QC and control charting techniques.

⁶ ASTM Manual MNL 7, *Manual on Presentation of Data Control Chart Analysis*, 6th ed., available from ASTM International Headquarters, International, W. Conshohocken, PA.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D 6732-01) that may impact the use of this standard.

- (1) Updated 1.1 and added a new Note 1.
- (2) Updated 4.1.
- (3) In 7.1.3, changed “accessory” to “atomizer.”
- (4) Added tolerance limits to 10 mL aliquots.
- (5) Updated 10.2.1 to state, “the intermediate stock standard and working standards shall be prepared daily.”
- (6) Updated Note 2.
- (7) Added new Fig. 2 and updated 14.1 to reference Fig. 2.
- (8) Added new Fig. 3 and updated 15.1 to reference Fig. 3.
- (9) Replaced “char cycle” with “char step” in Footnote B, Table 1.

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