INTERNATIONAL

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Standard Test Method for Determination of Copper in Jet Fuels by Graphite Furnace Atomic Absorption Spectrometry[1]

This standard is issued under the fixed designation D6732; 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~~5 µg/kg to ~~100~~100 µg/ ~~µg/kg~~ kg using graphite furnace atomic absorption spectrometry. Copper contents above ~~100~~100 µg/ ~~µg/kg~~ kg may be determined by sample dilution with kerosine to bring the copper level into the aforementioned method range. When sample dilution is used, the precision statements do not apply.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this 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:*[2]

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4306 Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination

D6299 Practice for Applying Statistical Quality Assurance and Control Charting Techniques to Evaluate Analytical Measurement System Performance

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 The graphite furnace is aligned in the light path of the atomic absorption spectrometer equipped with background correction. An aliquot (typically ~~10 µL)~~ 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.

[1] This test method is under the jurisdiction of ASTM Committee D02 on Petroleum ~~Products~~ Products, Liquid Fuels, and Lubricantsand is the direct responsibility of Subcommittee D02.03 on Elemental Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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~~50 µg⁄ ~~µg/kg)~~ 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,~~ 324.8 nm, setting the slit width at typically ~~0.7 nm,~~ 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~~ 324.8 nm wavelength range.

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

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

7.3 *Analytical Balance*—capable of weighing ~~100 g ± 0.0001 g.~~100 g ± 0.0001 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 specifications are available.[3] 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 Kerosine,* filtered through silica gel.

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

8.4 *Silica Gel,* ~~100~~100 mesh to ~~200 mesh.~~200 mesh.

8.5 *Argon Gas,* ~~*99.999%,*~~*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 kerosine 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 D4057.

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~~1 mg⁄ ~~mg/kg~~ kg Intermediate Stock Standard*—Accurately weigh a nominal ~~0.50 g~~ 0.50 g of the ~~100~~100 mg⁄ ~~mg/kg~~ kg stock organo-metallic standard into a suitable container (capable of being sealed for mixing). (All masses are measured to the nearest ~~0.0001 g.)~~ 0.0001 g.) Suitable sample containers are described in Practice D4306. Add enough odorless kerosine to bring the total mass to a nominal ~~50.00 g.~~ 50.00 g. Seal the container and mix well. See 12.1.1 for calculation of actual concentration.

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[3] *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.

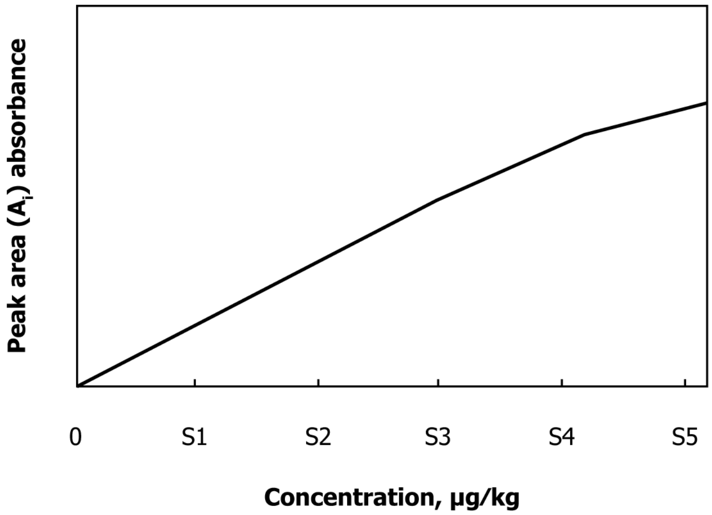

FIG. 1 Typical Calibration Curve of Copper Concentration versus Integrated Absorbance (A_i)

10.1.2 *Working Standards of Nominally ~~20,~~(20, 40, 60, 80, ~~and~~ 100) µg ~~100~~ / ~~µg/kg~~ kg*—Accurately weigh a nominal ~~0.20,~~(0.20, 0.40, 0.60, 0.80, ~~and 1.00 g~~ 1.00) g of the nominal ~~1~~1 mg/ ~~mg/kg~~ kg intermediate stock standard into five suitable containers. (All masses are measured to the nearest ~~0.0001 g.)~~ 0.0001 g.) Add enough odorless kerosine to each container to bring the total mass to a nominal ~~10.00 g.~~ 10.00 g. Seal containers and mix well. This produces working standards of nominal ~~20,~~(20, 40, 60, 80, ~~and~~100) µg/ ~~100 µg/kg,~~ 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 kerosine as a blank and each of the five working standards. The instrument measures the integrated absorbance A_i of ~~10 µL~~ 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*)~~*y*-axis) versus the concentrations of copper in the working standards in µg/kg (on ~~*x-axis*).~~*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~~ 324.8 nm and a slit width of typically ~~0.7 nm.~~ 0.7 nm. Align the hollow cathode lamp and 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 kerosine 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~~ 10 µL aliquot of odorless kerosine as a blank and then ~~10 µL~~ 10 µL of each of the standards onto the platform in the graphite tube. Then pipette ~~10 µL~~ 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 1—Aliquots other than ~~10 µL~~ 10 µL may be pipetted into the furnace. Volumes from ~~5~~5 µL to ~~40 µL~~ 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, 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~~1 mg/ ~~mg/kg~~ kg intermediate stock standard as follows:

$$c_i = c_s\, m_s / m_t \tag{2}$$