

This document is not an ASTM standard and is intended only to provide the user of an ASTM standard an indication of what changes have been made to the previous version. Because it may not be technically possible to adequately depict all changes accurately, ASTM recommends that users consult prior editions as appropriate. In all cases only the current version of the standard as published by ASTM is to be considered the official document.



Designation: D 3605 – 91 (Reapproved 1995)



Standard Test Method for Trace Metals in Gas Turbine Fuels by Atomic Absorption and Flame Emission Spectroscopy¹

This standard is issued under the fixed designation D 3605; 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 This test method is under the jurisdiction of ASTM Committee ~~D-2~~ D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D 02.03.0B on Spectrometric Methods.

Current edition approved ~~May 15, 1991~~, Aug. 10, 2000. Published ~~July 1991~~, August 2000. Originally published as D 3605 – 77. Last previous edition D 3605 – 87 91 (1995)^{ε1}.

1. Scope

1.1 This test method covers the determination of sodium, lead, calcium, and vanadium in Specification D 2880 Grade Nos. 1-GT and 2-GT fuels in the range from 0.1 to 2.0 mg/L. This test method is intended for the determination of oil-soluble metals and not waterborne contaminants in oil-water mixtures.

1.2 The preferred units are milligrams per litre.

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:*

D 2880 Specification for Gas Turbine Fuel Oils²

D 4057 Practice for Manual Sampling of Petroleum and Petroleum Products³

3. Summary of Test Method

3.1 The samples are prepared to conform with the requirements of the method of standard additions, which is selected to obviate problems encountered with the direct analysis of typical gas turbine fuels that exhibit significant variations in physical properties. Different, but known, amounts of analyte are added to two portions of sample. These, together with the unaltered sample, are burned in the flame of an atomic absorption instrument that measures light absorption by the atomized metals. The analysis of the sample portions with added analyte provides the calibration information necessary to calculate the analyte content of the unaltered sample.

3.2 Lead is determined by atomic absorption in a premixed air-acetylene flame, and sodium is determined by atomic absorption or atomic emission in a premixed air-acetylene flame. Calcium and vanadium are determined by atomic absorption or atomic emission in a premixed nitrous oxide-acetylene flame.

3.3 Most experience with this test method has been in the atomic absorption mode, although flame emission has been used successfully. Details in the subsequent sections are written for the atomic absorption mode. If the flame emission mode is used, minor details in the subsequent sections must be altered to conform to standard practice for flame emission spectroscopy. The precision statement applies only to the atomic absorption mode.

NOTE 1—Some GT fuel users may wish to determine potassium in addition to other metals included in this method. Potassium can be determined in a manner similar to that for sodium using a potassium hollow cathode lamp, (unless flame emission mode is used) a wavelength of 766.4 nm, and an appropriate organo-potassium standard. Precision data for potassium have not been determined.

4. Significance and Use

4.1 Knowledge of the presence of trace metals in gas turbine fuels enables the user to predict performance and, when necessary, to take appropriate action to prevent corrosion.

² *Annual Book of ASTM Standards*, Vol 05.021.

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 ASTM Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD: Vol 05.02.

5. Apparatus

5.1 *Atomic Absorption Spectrophotometer*, capable of measuring radiation over the wavelength range from 280 to 600 nm. The instrument must be capable of measuring low-level signals (approximately 1 % absorption or 0.004 absorbance unit per mg/L vanadium). The instrument should also be equipped as follows.

5.1.1 *Burner*, with variable nebulizer and auxiliary oxidant supply to reduce nonatomic absorption from unburned hydrocarbons which cause interferences.

5.1.1.1 *Burner Head*, capable of supporting a nitrous oxide-acetylene flame.

5.1.1.2 *Burner Head*, single- or multiple-slot, capable of supporting an air-acetylene flame.

5.1.2 *Electronic Detection System*, capable of reading to the nearest 0.1 % absorption or 0.0004 absorbance.

5.1.2.1 The text describes the measurement of absorption signals that is, either percent absorption or absorbance. For instruments reading in percent absorption, absorption signals of 0.1 % absorption must be measurable. For instruments reading in absorbance, signals of 0.0004 absorbance must be measurable.

5.1.3 *Hollow Cathode Lamp Power Supply*, regulated to minimize drift.

5.1.4 *Monochromator*, capable of resolving the 318.34–318.40-nm vanadium doublet from the 318.54-nm vanadium line.

5.1.5 *Hollow Cathode Lamps*, one each for calcium, sodium, lead, and vanadium.

NOTE 2—Electrodeless-discharge lamps can be an acceptable alternative, but the precision of this method was determined with hollow cathode lamps.

5.1.6 When the instrument has flame-emission capability, the emission technique can be used for the analyses of sodium, calcium, and vanadium.

5.2 *Volumetric Flasks*, 25-mL.

5.3 *Glass Vials*, 40-mL, screw-cap type, polyethylene-lined caps.

5.4 *Syringe*, 100- μ L, Hamilton type or equivalent.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in 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.⁴ Other grades may be used, provided it is ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 *1,2,3,4-tetrahydronaphthalene*⁵, practical grade, analyte-sterile.

NOTE 3—Analyte-sterile 1,2,3,4-tetrahydronaphthalene can be prepared by extracting a portion of tetralin with an equal amount of hydrochloric acid in a covered screw-cap vial. Heat the vial on a steam bath for 1 h and shake the vial for 1 h. If the acid extracted 1,2,3,4-tetrahydronaphthalene and unextracted 1,2,3,4-tetrahydronaphthalene give indistinguishable absorption signals for each of the analytes under optimal experimental conditions, the unextracted 1,2,3,4-tetrahydronaphthalene can be used throughout this method.

6.3 *Organometallic Standards*—Oil-soluble salts of sodium, lead, calcium, and vanadium of known concentration.⁶

6.4 *Mixed Standard*—Prepare a mixed standard containing 250 mg/L each of sodium, lead, calcium, and vanadium by dissolving the appropriate amounts of organometallic standards in 1,2,3,4-tetrahydronaphthalene and making the required dilutions. Prepare fresh daily, as needed.

7. Sampling

7.1 Samples shall be taken in accordance with the instructions in Practice D 4057.

8. Procedure

8.1 Fill two clean 25-mL volumetric flasks to the line with sample. With the microlitre syringe add 50 μ L of mixed standard to one flask and 100 μ L to the other. Touch the needle of the syringe to the inner wall of the flask to ensure quantitative transfer of the standard. Invert and mix the contents. (The two flasks are now spiked with 0.5 mg/L and 1.0 mg/L of sodium, lead, calcium, and vanadium). Alternatively, weigh 25.0 g of sample into each of two clean disposable glass vials and add the standard in the same manner. (The two vials are now spiked with 0.5 mg/kg and 1.0 mg/kg of sodium, lead, calcium, and vanadium.)

⁴ Tetralin (1,2,3,4-tetrahydronaphthalene), manufactured

⁴ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by E. I. duPont de Nemours the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and Co., has been found satisfactory; the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

⁵ Conostan standards, available from Conostan Division, Continental Oil Co., Ponca City, OK 74601, were used in determining the precision quoted in this method. Other standards are available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Institute of Standards

⁵ Tetralin (1,2,3,4-tetrahydronaphthalene), manufactured by E. I. duPont de Nemours and Technology, Washington, DC 20234, and from Angstrom, Inc., P. O. Box 252, Belleville, MI 48111, but the precision statement may or may not apply to results obtained with these standards. Co., has been found satisfactory.

⁶ Conostan standards, available from Conostan Division, Continental Oil Co., Ponca City, OK 74601, were used in determining the precision quoted in this method. Other standards are available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Institute of Standards and Technology, Washington, DC 20234, and from Angstrom, Inc., P. O. Box 252, Belleville, MI 48111, but the precision statement may or may not apply to results obtained with these standards.

8.2 Prepare a third spiked sample by adding approximately 1 mL of the mixed standard to approximately 25 mL of sample. This solution serves only to aid in establishing satisfactory operating conditions for the atomic absorption instrument.

8.3 Establish the atomic absorption instrument operating conditions, which are recommended by the manufacturer, and consider the following special points. Select the mode, flame gases, and spectral lines from the information presented in Table 1.

8.4 Analysis:

8.4.1 With the atomic absorption instrument in operation for monitoring lead absorption and with 1,2,3,4-tetrahydronaphthalene nebulizing, zero the instrument. Aspirate into the flame the third spiked sample described in 8.2 and note the net lead absorption signal. Optimize experimental conditions by adjusting the burner position (relative to the hollow cathode beam), the flow rates of the fuel and oxidant gases, and the sample aspiration rate until the net lead absorption signal maximizes. Re-zero the instrument with 1,2,3,4-tetrahydronaphthalene nebulizing, and consecutively introduce into the flame the unaltered sample and the two spiked samples, with 1,2,3,4-tetrahydronaphthalene nebulizing between each sample. Record the absorption signal of each sample and of each blank between samples.

8.4.1.1 At optimal experimental conditions, the analyte concentration that accounts for 1 % absorption should be approximately 1 mg/L. The percent absorption to concentration ratio must be near unity in order to achieve the lower limits of detection that are required. This note does not apply to flame emission measurements.

8.4.2 With the atomic absorption instrument in operation for monitoring vanadium absorption and with 1,2,3,4-tetrahydronaphthalene nebulizing, zero the instrument. Introduce into the flame the third spiked sample described in 8.2. Record the net vanadium absorption signal. Optimize the experimental conditions as in 8.4.1. Re-zero the instrument with 1,2,3,4-tetrahydronaphthalene nebulizing and consecutively introduce into the flame the unaltered sample and the two spiked samples. Record the absorption signal of each sample and of each 1,2,3,4-tetrahydronaphthalene blank between samples.

8.4.3 With the atomic absorption instrument in operation for monitoring sodium absorption, zero the instrument with 1,2,3,4-tetrahydronaphthalene nebulizing, and consecutively introduce into the flame the unaltered sample and the two spiked samples. Record the absorption signal of each sample and of each 1,2,3,4-tetrahydronaphthalene blank between samples.

NOTE 4—For determining sodium and calcium, the maximization of absorption or emission signals is not critical.

8.4.4 With the atomic absorption instrument in operation for monitoring calcium absorption, zero the instrument with 1,2,3,4-tetrahydronaphthalene nebulizing, and consecutively introduce into the flame the unaltered sample and the two spiked samples. Record the absorption signal of each sample and of each 1,2,3,4-tetrahydronaphthalene blank between samples.

9. Calculation

9.1 For each absorption signal, calculate the net absorption signal as follows:

$$a = A - [(b_1 + b_2)/2] \quad (1)$$

where:

a = net absorption signal,

A = observed absorption signal,

b_1 = blank signal before the sample, and

b_2 = blank signal after the sample.

NOTE 5—Blank corrections are usually small. If a large drift in blank signals is observed during a series of measurements, some experimental parameter is out of control. The cause of the variation should be corrected, and the measurements repeated.

9.2 For each element in turn, calculate sensitivities as follows:

$$S_{0.5} = 2 (a_1 - a_2) \quad (2)$$

$$S_{1.0} = (a_3 - a_2) \quad (3)$$

$$S = (S_{0.5} + S_{1.0})/2 \quad (4)$$

TABLE 1 Experimental Conditions

Element	Mode	Wavelength, nm	Fuel	Oxidant
Na	Absorption	589.6	C ₂ H ₂	air
Na	Emission	589.6	C ₂ H ₂	air
Pb	Absorption	283.3	C ₂ H ₂	air
Ca	Absorption	422.7	C ₂ H ₂	N ₂ O
Ca	Emission	422.7	C ₂ H ₂	N ₂ O
V	Absorption	318.34–318.40	C ₂ H ₂	N ₂ O
V	Emission	437.9	C ₂ H ₂	N ₂ O

where:

- $S_{0.5}$ = sensitivity for the 0.5-mg/L spiked sample,
- $S_{1.0}$ = sensitivity for the 1.0-mg/L spiked sample,
- S = average sensitivity,
- a_1 = net absorption signal for the 0.5-mg/L spiked sample,
- a_2 = net absorption signal for the unaltered sample, and
- a_3 = net absorption signal for the 1.0-mg/L spiked sample.

9.3 Calculate the ratio of sensitivities, R , as follows:

$$R = S_{1.0}/S_{0.5} \quad (5)$$

If R falls outside the range of $0.90 \leq R \leq 1.10$, the data are nonlinear. Readjust experimental conditions and repeat the analysis.

9.4 Calculate the concentration of each element as follows:

$$\text{mg/L} = a_2/S \quad (6)$$

$$\text{mg/kg} = a_2/(S \times d) \quad (7)$$

where d = density of the sample in g/ml.

10. RepQuality Control Checks (QA/QC)

10.1 When QA/QC protocols are already established in the testing facility, these may be used to confirm the reliability of the test method.

10.2 Since reference materials for the various matrices are not available and the test method utilizes the method of standard additions, the only practical quality control check is to verify the nearest 0.1 mg/L accuracy of the organometallic standard in 6.3. A source independent of this standard should be acquired and a sample carried through the analysis using the second-source standard as the known addition. Results of this test can be compared to the original sample result using the original standard material to verify accuracy.

11. Report

11.1 Report results for each element to the nearest 0.1 mg/L.

12. Precision and Bias

12.1 The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

12.1.1 *Repeatability*—The difference between successive test 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 in one case in twenty:

Element	Repeatability
V	0.452 (concentration) ^{1/2}
Pb	0.244 (concentration) ^{1/2}
Ca	0.202 (concentration) ^{1/2}
Na	0.232 (concentration) ^{1/2}

12.1.2 *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, in the normal and correct operation of the test method exceed the following values only in one case in twenty:

Element	Reproducibility
V	0.616 (concentration) ^{1/2}
Pb	0.900 (concentration) ^{1/2}
Ca	0.402 (concentration) ^{1/2}
Na	0.738 (concentration) ^{1/2}

NOTE 6—The above repeatability and reproducibility are based on a concentration range of 0.1 to 0.5 mg/L and apply only to the atomic absorption mode.

12.2 *Bias*—The bias of this test method cannot be determined since appropriate reference materials containing known levels of vanadium, lead calcium and sodium are not available.

123. Keywords

123.1 atomic absorption; calcium; flame emission; gas turbine fuels; lead; sodium; vanadium

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org).