Designation: D7151 – 13 D7151 – 15

Standard Test Method for
Determination of Elements in Insulating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)[1]

This standard is issued under the fixed designation D7151; 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 describes the determination of metals and contaminants in insulating oils by inductively coupled plasma atomic emission spectrometry (ICP-AES). The specific elements are listed in Table 1. This test method is similar to Test Method D5185, but differs in methodology, which results in the greater sensitivity required for insulating oil applications.

1.2 This test method uses oil-soluble metals for calibration and does not purport to quantitatively determine insoluble particulates. Analytical results are particle size dependent, and low results are obtained for particles larger than several micrometers.[2]

1.3 This test method determines the dissolved metals (which can originate from overheating or arcing, or both) and a portion of the particulate metals (which generally originate from a wear mechanism). While this ICP method detects nearly all particles less than several micrometers, the response of larger particles decreases with increasing particle size because larger particles are less likely to make it through the nebulizer and into the sample excitation zone.

1.4 This test method includes an option for filtering the oil sample for those users who wish to separately determine dissolved metals and particulate metals (and hence, total metals).

1.5 Elements present at concentrations above the upper limit of the calibration curves can be determined with additional, appropriate dilutions and with no degradation of precision.

1.6 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.7 *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 to determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[3]

C1109 Practice for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy

D923 Practices for Sampling Electrical Insulating Liquids

D1744 Test Method for Water in Liquid Petroleum Products by Karl Fischer Reagent[4]

D2864 Terminology Relating to Electrical Insulating Liquids and Gases

D4307 Practice for Preparation of Liquid Blends for Use as Analytical Standards

D5185 Test Method for Multielement Determination of Used and Unused Lubricating Oils and Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

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[1] This test method is under the jurisdiction of ASTM Committee D27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.03 on Analytical Tests.

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[2] Eisentraut, K. J., Newman, R. W., Saba, C. S., Kauffman, R. E., and Rhine, W. E., *Analytical Chemistry*, Vol 56, 1984.

[3] 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.

[4] Withdrawn. The last approved version of this historical standard is referenced on www.astm.org.

TABLE 1 Elements Determined and Suggested Wavelengths[A]

Element	Wavelength, nm
Aluminum	308.22, 396.15, 309.27
Cadmium	226.50. 214.44
Cobalt	228.62 231.16
Copper	324.75
Iron	259.94, 238.20
Lead	220.35
Nickel	231.60, 227.02, 221.65
Scandium	361.38
Silicon	288.16, 251.61
Silver	328.07
Sodium	589.59
Tin	189.99, 242.95
Tungsten	239.71
Yttrium	371.03
Zinc	206.20, 202.55, 213.86, 334.58, 481.05

[A]These wavelengths are only suggested and do not represent all possible choices.

3. Terminology

3.1 Definitions for general terms are found in Terminology D2864.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *Babington-type nebulizer, n*—a device that generates an aerosol by flowing a liquid over a surface that contains an orifice from which gas flows at a high velocity.

3.2.2 *inductively-coupled plasma (ICP), n*—a high-temperature discharge generated by flowing an ionizable gas through a magnetic field induced by a load coil that surrounds the tubes carrying the gas.

3.2.3 *linear response range, n*—the elemental concentration range over which the calibration curve is a straight line, within the precision of the test method.

3.2.4 *profiling, n*—a technique that determines the wavelength for which the signal intensity measured for a particular analyte is a maximum.

3.2.5 *wear metal, n*—an element introduced into the oil by wear of oil-wetted parts.

3.2.6 *dissolved metal, n*—a metallic element in the oil which will pass a 0.45 μm filter.

4. Summary of Test Method

4.1 A weighed portion of a thoroughly homogenized insulating oil is diluted by weight with kerosine or other suitable solvent. Standards are prepared in the same manner. An internal standard may be added to the solutions to compensate for variations in test specimen introduction efficiency. The solutions may be introduced to the ICP instrument by a peristaltic pump. If free aspiration is used, an internal standard shall be used. By comparing emission intensities of elements in the test specimen with emission intensities measured with the standards, the concentrations of elements in the test specimen are calculated.

5. Significance and Use

5.1 This test method covers the rapid determination of 12 elements in insulating oils, and it provides rapid screening of used oils for indications of wear. Test times approximate several minutes per test specimen, and detectability is in the 10 through 100 μg/kg range.

5.2 This test method can be used to monitor equipment condition and help to define when corrective action is needed. It can also be used to detect contamination such as from silicone fluids (via Silicon) or from dirt (via Silicon and Aluminum).

5.3 This test method can be used to indicate the efficiency of reclaiming used insulating oil.

6. Interferences

6.1 *Spectral*—Check all spectral interferences expected from the elements listed in Table 1. Follow the ICP manufacturer's operating guide to develop and apply correction factors to compensate for the interferences. To apply interference corrections, all concentrations must be within the previously established linear response range of each element listed in Table 1.

6.1.1 Spectral interferences can usually be avoided by judicious choice of analytical wavelengths. When spectral interferences cannot be avoided, the necessary corrections shall be made using the computer software supplied by the ICP manufacturer or the empirical method given in Test Method C1109 or by Boumans.[5]

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[5] Boumans, P. W .J. M., "Corrections for Spectral Interferences in Optical Emission Spectroscopy with Special Reference to the RF Inductively Coupled Plasma," *Spectrochimica Acta*, 1976, Vol 318, pp. 147-152.

6.1.2 Interference correction factors can be negative if off-peak background correction is employed for an element. A negative correction factor can result when an interfering line is encountered at the background correction wavelength rather than at the peak wavelength.

6.2 *Viscosity Effects*—Differences in the viscosities of the test specimen solutions and standard solutions can cause differences in the uptake rates. These differences can adversely affect the accuracy of the analysis. The effects can be reduced by using a peristaltic pump to deliver solutions to the nebulizer or by the use of internal standardization, or both.

6.3 *Particulates*—The use of an internal standard will reveal when particulates cause flow problems. Use of a Babington-type high-solids nebulizer helps to minimize plugging of the nebulizer. Also, the specimen introduction system can limit the transport of particulates, and the plasma can incompletely atomize larger particulates, thereby causing low results.

6.4 *Solvent Moisture*—Excessive moisture (>30 mg/kg) in the kerosine used for dilution can cause poor recovery of some elements. This can be minimized by checking each lot of kerosine for moisture content using Test Method D1744 and by analyzing all diluted standards and test specimens within 24 h of preparation.

7. Apparatus

7.1 *Balance,* top loading, with automatic tare, capable of weighing to 0.001g, capacity of at least 150 g. A balance with a capacity of at least 250 g is required if preparing the Internal Standard according to 10.2.

7.2 *Inductively Coupled Plasma Atomic Emission Spectrometer*—Either a sequential or simultaneous spectrometer is suitable, if equipped with a quartz ICP torch and RF generator to form and maintain the plasma. Suggested wavelengths for the determination of the elements in insulating oil are given in Table 1.

7.3 *Nebulizer*—Use the nebulizer recommended by the ICP manufacturer. A Babington-type high-solids nebulizer should be used if samples contain high solids. This type of nebulizer reduces the possibility of clogging and minimizes aerosol particle effects.

7.4 *Peristaltic Pump,* (optional)—A peristaltic pump may be used to provide a constant flow of solution. The pump tubing shall be able to withstand at least 6 h exposure to the dilution solvent. Viton tubing is typically used with hydrocarbon solvents, and poly (vinyl chloride) tubing is typically used with methyl isobutyl ketone.

7.5 *Solvent Dispenser* (optional),— A solvent dispenser calibrated to deliver the required weight of dilution solvent is very useful. This dispenser shall have at least 1 % accuracy and 0.1 % precision.

7.6 *Internal Standard Dispenser* (optional),— A dispenser calibrated to deliver the required weight of internal standard solution is very useful. This dispenser shall have at least 1 % accuracy and 0.1 % precision.

7.7 *Specimen Solution Containers,* nominal 30-mL glass or polyethylene vials, with screw caps or snap-top caps.

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.[6] 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 determination.

8.2 *Base Oil*—U.S.P. White oil or any mineral oil that is free of analytes and having a viscosity at room temperature as close as possible to that of the samples to be analyzed.

8.3 *Dilution Solvent*—Reagent grade kerosine is recommended as a dilution solvent. Another solvent (such as toluene or xylene) may be used if it is free of all analytes and completely dissolves all standards and samples.

8.4 *Internal Standard*—Oil-soluble scandium, cobalt, or yttrium is required when the internal standardization option is selected.

8.5 *Organometallic Standards*—Multi-element standards, containing 3.0 and 10.0 ~~µg/g~~mg/kg of each element, can be purchased or prepared from the individual concentrates. Refer to Practice D4307 for a procedure for preparation of multicomponent liquid blends. When preparing multi-element standards, an ultrasonic bath is recommended to ensure that complete mixing is achieved. It is highly recommended to purchase the standards because of the difficulty in preparing multi-element standards.

9. Hazards

9.1 Kerosine is classified as a combustible liquid and must be kept away from all ignition sources. If the ICP is allowed to operate unattended, equipment malfunctions could cause leakage of kerosine.

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[6] *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.

10. Internal Standardization

10.1 The internal standard procedure requires that every test specimen solution have the same concentration of an internal standard element that is not present in the original specimen. Specimen to specimen changes in the emission intensity of the internal standard element can be used to correct for variations in the test specimen introduction efficiency, which is dependent on the physical properties of the test specimen.

10.2 *Internal Standard Solution* —Weigh 25.0 ± 0.1g of 2000 ~~μg/g~~mg/kg scandium-in-oil (or cobalt- or yttrium-in-oil) standard into a 500-mL Erlenmeyer flask. Add kerosine to make a total of 250 ± 1 g. Mix this solution thoroughly and transfer to the reservoir for the internal standard container or dispenser. The concentration of the internal standard is not required to be 200 ~~μg/g~~ mg/kg. However, the concentration of the internal standard element should be at least 100 times its detection limit.

11. Sampling and Sample Handling

11.1 Laboratory samples must be taken in accordance with the instructions in Practices D923.

11.2 It is important to homogenize the insulating oil in the sample container in order to obtain a representative test specimen. Mix the insulating oil sample vigorously by inverting several times.

11.3 (Optional) To separately determine the dissolved metals and particulate metals, filter the oil sample through a 0.45 μm filter. The particles on the filter paper must then be dissolved or digested by a technique not addressed by this test method.

12. Preparation of Test Specimens and Standards

12.1 All test specimens and standards must be mixed thoroughly when diluted with kerosine and the internal standard. They must all be prepared utilizing the same batch of internal standard. All prepared solutions must be analyzed within 24 h of preparation.

12.2 *Blank*—Prepare a blank by adding 6.00 ± 0.02 g base oil, 1.00 ± 0.01 g internal standard solution, and 8.00 ± 0.03 g kerosine to a 30-mL vial.

12.3 *Working Standard*—Prepare a calibration standard by adding 6.00 ± 0.02 g of the 10 ~~μg/g~~mg/kg multi-element standard, 1.00 ± 0.01 g internal standard solution, and 8.00 ± 0.03 g kerosine to a 30-mL vial.

12.4 *Check Standard*—Prepare a QC check standard by adding 6.00 ± 0.02 g of the 3.0 ~~μg/g~~mg/kg multi-element standard, 1.00 ± 0.01 g internal standard solution, and 8.00 ± 0.03 g kerosine to a 30-mL vial. Other concentrations may be used for the check standard as long as they are not prepared from the 10 ~~μg/g~~mg/kg standard used for calibration.

12.5 *Test Specimen*—Add 6.00 ± 0.02 g of a well-homogenized sample, 1.00 ± 0.01 g internal standard solution, and 8.00 ± 0.03 g kerosine to a 30-mL vial. If the analysis report indicates a concentration above the linear range, prepare a 10-fold dilution by adding 0.60 ± 0.01 g of the sample, 5.40 ± 0.02 g base oil, 1.00 ± 0.01 g internal standard solution, and 8.00 ± 0.03 g kerosine to a 30-mL vial. Identify the sample as a 10X dilution and ensure that the instrument software will correct the concentrations for the additional dilution.

13. Preparation of Apparatus

13.1 *Instrument*—Design differences between instruments, ICP excitation sources, and different selected analytical wavelengths for individual spectrometers make it impractical to detail the operating conditions. Consult the manufacturer's instructions for operating the instrument with organic solvents. Set up the instrument for use with the particular dilution solvent chosen.

NOTE 1—For some ICP detectors, response for some elements may vary with changing temperature. The instrument should be in a constant-temperature environment during the analysis of a batch of specimens.

13.2 *Peristaltic Pump*—If a peristaltic pump is used, inspect the pump tubing and replace it, if necessary, before starting each day. (See 7.4 for the proper types of tubing.) Verify the solution uptake rate and adjust it to the desired rate.

13.3 *ICP Excitation Source*—Initiate the plasma source at least 30 min before performing analysis. During this warm up period, nebulize dilution solvent. Inspect the torch for carbon build-up during the warm-up period. If carbon build-up occurs, consult the manufacturer's operating guide to take proper steps to remedy the situation.

NOTE 2—Some manufacturers recommend even longer warm-up periods to minimize changes in the slopes of calibration curves.

13.4 *Wavelength Profiling*—Perform any wavelength profiling that may be called for in the normal operation of the instrument.

13.5 *Operating Parameters*—Assign the appropriate operating parameters to the instrument task file so that the desired elements can be determined. Parameters to be included are element, wavelength, background correction points (optional), interelement correction factors (optional), integration time, and internal standard correction (optional). Multiple integrations are required for each measurement.

14. Calibration and Standardization

14.1 The linear range must be established once for the particular instrument being used. This is accomplished by running intermediate standards between the blank and the working standard and by running standards containing higher concentrations than the working standard. Analyses of test specimen solutions must be performed within the linear range of response.

14.2 *Working Standard*—At the beginning of the analysis of each batch of specimens, perform a two-point calibration consisting of the blank and working standard. Use the check standard to determine if each element is in calibration. When the results obtained with the check standard are within 10 % of the expected concentrations for all elements, proceed with test specimen analyses. Otherwise, make any adjustments to the instrument that are necessary and repeat the calibration. Repeat this procedure with the check standard at least every fifteen samples.

14.3 *Working Standard with Internal Standard*—Calibrate the instrument as described in 14.2. Obtain a printed record of the standard's emission intensities and those of the internal standard. Calculate an intensity ratio for each element by the following equation:

$$I(Re) = \frac{I(e) - I(Be)}{I(is)}$$

(1)

where:

$I(Re)$ = intensity ratio for element *e*,
$I(e)$ = intensity for element *e*,
$I(Be)$ = intensity of the blank for element *e*, and
$I(is)$ = intensity of internal standard element.

14.3.1 Calculate the calibration factors from the intensity ratios. Alternatively, use the computer programs provided by the instrument's manufacturer to calibrate the instrument using internal standardization.

15. Procedure and Calculation

15.1 *Analysis*—Analyze the test specimen solutions in the same manner as the calibration standards (that is, same integration time, background correction points, plasma conditions, etc.). Between test specimens, nebulize dilution solvent for at least 30 s. Calculation of concentrations can be performed manually or by computer when such a feature is available. Correct the concentrations of any test specimens diluted additionally.

NOTE 3—If the repeatability is not acceptable for a given application of the results, then the analyses of the specimens can be performed in duplicate or triplicate and the average reported. When low detection limits (such as those indicated in Table 2) are desired, triplicate analyses may be required.

15.2 *Quality Control with Check Standard*—Analyze the check standard at least after every fifteen specimens. If any result is not within 10 % of the expected concentration, recalibrate the instrument and reanalyze the test specimens solutions back to the previous acceptable check standard analysis.

15.3 *Analysis with Internal Standardization*—Analyze the test specimen solutions and calculate an intensity ratio for each of the elements found in the test specimen solutions using Eq 1 given in 14.3. From the intensity ratios, concentrations of the elements can be calculated.

16. Report

16.1 Report the following information: elemental concentrations to the nearest 0.01 ~~µg/g~~mg/kg but with no more than three significant figures. Concentrations for elements not detected shall be reported as less than their detection limit. Typical detection limits are shown in Table 2.

NOTE 4—Some problems in electrical equipment filled with insulating oil might not be detected at these detection limits.

TABLE 2 Typical Detection Limits (using the average of triplicate trials)

Element	Detection Limit (~~µg/g~~)(mg/kg)
Aluminum	0.05
Cadmium	0.01
Copper	0.01
Iron	0.03
Lead	0.05
Nickel	0.04
Silicon	0.05
Silver	0.01
Sodium	0.05
Tin	0.1
Tungsten	0.04
Zinc	0.01

17. Precision and Bias[7]

17.1 ~~Precision—An estimate of precision by standard deviation has been determined by one laboratory for 7 replicates of a fluid containing a nominal 1 ppm by weight and is shown in~~The precision of this test method is based on an interlaboratory study of ASTM D7151, Standard Test Method for Determination of Elements in Insulating Oils by Inductively Coupled Plasma Atomic ~~Table 3. The repeatability and reproducibility of this test method is being determined~~ Emission Spectrometry (ICP-AES), conducted in 2013. Seven laboratories participated in this study, testing eighteen different oils for up to twelve different metals. Every "test result" represents an individual determination. The laboratories were asked to report three test results for each oil / dissolved metals combination. Practice E691~~and will be available on or before December 31, 2014.~~ was followed for the basic design and analysis of the data; the details are given in an ASTM Research Report.[7]

17.1.1 *Repeatability limit (r)*—Two test results obtained within one laboratory shall be judged not equivalent if they differ by more than the "*r*" value for that material; "*r*" is the interval representing the critical difference between two test results for the same material, obtained by the same operator using the same equipment on the same day in the same laboratory.

17.1.1.1 Repeatability limits are listed in Tables 3-14.

17.1.2 *Reproducibility limit (R)*—Two test results shall be judged not equivalent if they differ by more than the "*R*" value for that material; "*R*" is the interval representing the critical difference between two test results for the same material, obtained by different operators using different equipment in different laboratories.

17.1.2.1 Reproducibility limits are listed in Tables 3-14.

17.1.3 The above terms (repeatability limit and reproducibility limit) are used as specified in Practice E177.

17.1.4 Any judgment in accordance with 17.1.1 would normally have an approximate 95% probability of being correct, however the precision statistics obtained in this ILS must not be treated as exact mathematical quantities which are applicable to all circumstances and uses. The limited number of laboratories reporting results for some elements indicates that there will be times when differences greater than predicted by the ILS results will arise, sometimes with considerably greater or smaller frequency than the 95 % probability limit would imply. Consider the precision limits listed for those elements with fewer than six reporting laboratories as a general guide, and the associated probability of 95% as only an indicator of what can be expected.

17.2 ~~Bias—No information can be presented on the bias as no interlaboratory study has been completed. This information will be available on or before December 31, 2014.~~

18. Keywords

18.1 aluminum; cadmium; copper; emission-spectrometry; ICP; inductively coupled plasma atomic emission spectrometry; insulating liquid; iron; lead; silicon; silver; sodium; tin; transformer oil; tungsten; wear metals; zinc

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[7] ~~A research report is available from ASTM International Headquarters. Request~~ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report ~~RR:D27-1017~~RR:D27-1020. Contact ASTM Customer Service at service@astm.org.

TABLE 3 Zinc (ppm)—7 laboratories

Material	Average[A]	Repeatability Standard Deviation	Reproducibility Standard Deviation	Repeatability Limit	Reproducibility Limit
	$\bar{x}$	s_r	s_R	r	R
5.0 mg/kg Standard	4.77	0.35	0.88	0.98	2.45
3.7 mg/kg Standard	3.77	0.43	0.57	1.19	1.60
2.5 mg/kg Standard	2.60	0.21	0.54	0.59	1.52
1.5 mg/kg Standard	1.65	0.28	0.51	0.79	1.42
0.6 mg/kg Standard	0.78	0.20	0.30	0.56	0.84
0.3 mg/kg Standard	0.56	0.23	0.40	0.65	1.12

[A] The average of the laboratories' calculated averages.