Designation: D8371 – 20

Standard Test Method for Trace Metal Content Analysis in Carbon Black[1]

This standard is issued under the fixed designation D8371; 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 metal content in carbon black with ICP-OES or ICP-MS after adequate digestion. See 3.1.5 – 3.1.7 for definitions.

1.2 The concentration ranges covered by these test methods are determined by the sensitivity of the instruments, the amount of sample taken for analysis and the dilution volume.

1.3 Detection limits, sensitivity and optimum ranges of the metals will vary with the matrices and model of spectrometer.

1.4 Elements present at concentrations above the linear response range of the calibration curve can be determined with additional appropriate dilutions.

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

1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1193 Specification for Reagent Water

D1506 Test Methods for Carbon Black—Ash Content

D7260 Practice for Optimization, Calibration, and Validation of Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for Elemental Analysis of Petroleum Products and Lubricants

3. Terminology

3.1 *Definitions:*

3.1.1 *calibration, n*—the process by which the relationship between signal intensity and element concentration is determined for a specific element analysis.

3.1.2 *calibration curve, n*—the plot of signal intensity (on the 'y' axis) versus element concentration (on the 'x' axis) using data obtained from standards that contain certified trace metal concentrations (calibration solutions), known with high accuracy.

3.1.3 *calibration solution, n*—solution containing mixture of elements of known concentrations (multi element certified standard solution).

3.1.4 *detection limit, n*—the concentration of an analyte that results in a signal intensity that is some multiple (typically three) times the standard deviation of the background intensity of the blank.

3.1.5 *ICP-MS, n*—inductively coupled plasma – mass spectrometry.

3.1.6 *ICP-OES, n*—inductively coupled plasma – optical emission spectrometry.

3.1.7 *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.

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

3.1.9 *secondary solution, n*—calibration solution from a second source.

4. Summary of Test Method

4.1 A sample of carbon black is digested either with strong acid under high temperature and pressure or after incineration of the sample and acid treatment of the ash. By digestion, the trace metals are transferred into their soluble salts, and most of the interfering matrix components, that is, carbon black, are removed.

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[1] This test method is under the jurisdiction of ASTM Committee D24 on Carbon Black and is the direct responsibility of Subcommittee D24.66 on Environment, Health, and Safety.

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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.

4.2 The digestion solution is measured with an ICP-OES or ICP-MS to quantify the trace metals of interest, after a calibration with a mix of elements in a certified standard reference solution. The concentrations of elements in the test specimen are calculated by comparing emission intensities of elements in the test specimen with emission intensities measured in the standards.

4.3 The ICP-MS is typically one or more orders of magnitude more sensitive and has a wider dynamic range than ICP-OES. The quantitative reporting limits of the instruments in terms of ug/g sample varies with specific element, sample weight, final solution volume, specific instrument, and other factors. For example, for a 0.3 g sample weight into a final volume of 25 cm^3, ICP-MS for some transition elements can measure down to the 10's of ppb concentrations or possibly less, while both ICP-OES and ICP-MS can be used for measurements in the ppm range.

4.4 The instrument manufacturers recommendations should be followed when operating the ICP-OES or ICP-MS. Additional information and other general considerations on the ICP-OES technique are given in Practice D7260.

5. Significance and Use

5.1 This test covers the quantitation of trace metals in carbon black. The quantitation of heavy metals may help to estimate their contribution to a final finished article. Metal components may impact application properties of final products or may be a regulatory issue. It is the responsibility of the user of the material to consider the impact of the elements when designing a final product.

5.2 Elements which cannot be digested with nitric acid, such as silicon, cannot be quantified by this test method. This standard describes two digestion methods; microwave acid digestion and furnace ashing. The furnace ashing method may not be appropriate for certain more volatile elements which can be lost during incineration.

6. Apparatus

6.1 *Balance,* analytical, with 0.1 mg sensitivity.

6.2 *Microwave,* capable of producing 285°C and pressure of 16 MPa (160 bar). Microwaves with lower temperatures and pressures can be used provided the sample is adequately digested.

6.3 *Microwave Digestion Vessels with Lid* (made of quartz).

6.4 *50 cm^3 Polypropylene Tubes,* graduated.

6.5 *15 cm^3 Polypropylene Tubes,* graduated.

6.6 *Syringe Filter,* resistant to acids, for example, Teflon. Filter pore size used is dependent on nebulizer capability as recommended by the ICP manufacturer.

6.7 *Single-use Syringes,* 10 cm^3.

6.8 *ICP-OES or ICP-MS.*

6.9 *Muffle Furnace,* capable of temperature regulation of a minimum of 550°C ± 25°C.

6.10 *Crucibles,* made of porcelain, quartz or platinum, high-form, for example, size O, rim 35 mm, height 29 mm, capacity 15 cm^3, with cover. Other size crucibles may be used.

6.11 *Desiccator.*

6.12 *Oven,* gravity-convection type, capable of temperature regulation within ±1°C at 125°C and temperature uniformity within ±5°C.

6.13 *Filter Paper,* for example, Whatman #41.

7. Reagents and Solutions

7.1 Argon, purity 5.0.

7.2 Nitrogen, purity 5.0.

7.3 Water, ultra-pure with a conductivity according to Specification D1193 Type I.

7.4 Nitric acid (HNO_3) 67 to 69 %, supra pure or trace metal grade.

7.5 Hydrochloric acid (HCl), concentrated, trace metal grade or equivalent.

7.6 Multi-Element certified standard solutions.

7.7 Desiccant.

NOTE 1—All reagents should be of sufficiently high purity to permit their use without negatively impacting the accuracy of the determination.

8. Procedure

8.1 *Sample Preparation/Digestion*—The parameters described in 8.2.1 – 8.2.5 provide appropriate microwave digestion. Other microwave parameters can be used that shall provide adequate digestion of the trace metals. Ideally the obtained solution should be clear by visual observation. In some cases, a small amount of visible carbon black may remain after the microwave step and it would not be possible to determine visually if any undissolved metals are remaining. In those cases, the adequacy of the digestion shall be verified by comparing to the furnace ashing method (for non-volatile metals) and by achieving appropriate recoveries on a spiked sample.

8.2 *Method A – Microwave Digestion:*

NOTE 2—Microwave digestion of carbon black is a hazardous operation involving concentrated acids under high pressure and heat, generation of toxic vapors such as NOx, and other hazards. Follow the safety instructions by the manufacturer.

8.2.1 A sample amount of 0.3 to 0.4 g carbon black is weighed to the nearest 0.1 mg in a quartz digestion vessel, mixed with 10 cm^3 of nitric acid and covered with a lid.

8.2.2 Fill the reactor vessel with 120 cm^3 water.

8.2.3 Place the reactor vessel and the sample rack into the microwave device.

8.2.4 Start a temperature ramp program going to 285°C at a pressure of 16 MPa (160 bar).

8.2.5 Hold the final temperature and pressure for 30 min.

8.2.6 Quantitively bring the volume of the solution obtained in 8.2.5 up to 25 cm^3 using water and transfer the required amount into an ICP tube for testing. Other volumes can be used.

NOTE 3—For sensitive nebulizers it might be required to filter the solution prior to testing. Pull approximately 10 cm^3 of this solution into a syringe and filter through a syringe filter into an ICP tube.

8.3 *Method B – Digestion by Incineration:*

NOTE 4—This method should not be used for low volatility elements such as, for example Hg, Se, S, As, Cd, P unless recovery studies are performed.

8.3.1 Incinerate 5 g of the sample as described in Test Methods D1506.

NOTE 5—Higher sample amounts (up to 30 g), longer ashing times (up to 2 days) and higher temperatures (up to 600°C) can be used if needed to completely ash the sample.

8.3.2 Add concentrated HNO_3 and concentrated HCl in a ratio of 1:4 or 1:3 to the crucible containing the sample ash. The total volume added depends on the amount needed to dissolve the ash, final volume after dilution with water, and any limits needed on final concentration of the acid mixture that is injected into the ICP. For example, for a final diluted volume of 100 mL, 4 cm^3 of concentrated HNO_3 and 12 cm^3 of concentrated HCl can be added to the crucible containing the sample ash. However, much smaller volumes can be used if proven effective.

Warning—*Aqua Regia* is a very strong acid made by combining HNO_3 and HCl in a 1:3 ratio. This mixture is extremely corrosive and may generate hazardous fumes during sample dissolution. All appropriate care and safety precautions shall be taken when using strong mineral acids, including wearing proper personal protective equipment and sufficient ventilation.

8.3.3 Carefully heat the crucible containing the acid solution on a hotplate. Do not allow sample mixture to boil in order to prevent splashing or evaporation to dryness. Heat the sample for at least one hour until the sample dissolution is complete, indicated by a clear solution by visual observation. If solution is not clear, further investigation may be needed to determine the nature of the undissolved material, for example silica. Allow the solution to cool.

NOTE 6—If an internal standard, for example, Y reference solution, is used, add it during an appropriate step, for example, in step 8.3.4 before bringing the solution up to the final volume.

8.3.4 Carefully add approximately 10 cm^3 of deionized water (DI) to the crucible containing the digested solution.

8.3.5 If the solution is not to be filtered, proceed to 8.3.6. Otherwise, place paper filter specified in 6.13 into a funnel and filter the diluted solution into a volumetric flask (for example, 100 cm^3). Rinse the crucible and filter thoroughly with pure water, ensuring that all sample solution has been quantitatively removed from the crucible and transferred to the volumetric flask through the filter.

8.3.6 If the solution was filtered as specified in 8.3.5, dilute the solution to volume with pure water and mix the sample solution well before analysis. If the solution in the crucible was not filtered, quantitatively transfer from the crucible into a volumetric flask (for example, 100 cm^3) and dilute to volume.

8.4 *ICP-OES Measurement:*

NOTE 7—Design differences between instruments, ICP excitation sources and different selected analytical wavelengths for individual spectrometers and applications make it impractical to detail the operating conditions. Consult the manufacturer's instructions for the operation of the ICP instrument.

8.4.1 Prepare calibration solutions by diluting the standard reference solutions with the elements to be quantified in the test sample.

8.4.2 Set up the ICP-OES with all appropriate parameters as recommended by the manufacturer to achieve appropriate detection limits and precision.

8.4.3 Measure different wavelengths specifically for each element to detect spectral interferences. See Table 1.

8.4.4 The accuracy of the ICP measurement should be confirmed by running, as a sample check, a certified mix of elements that is preferably obtained from a different vendor (commonly referred to as the second source) than the vendor that supplies the primary certified mix of elements used to calibrate the instrument.

8.4.5 Check that each element is within the calibration range. Otherwise dilute the solution and measure again.

NOTE 8—It is advised to run a blank to obtain background information. With any instrument, the analyst must always be cautious of the possible presence of unexpected elements producing interfering spectral lines.

8.5 *ICP-MS Measurement:*

NOTE 9—Design differences between instruments and applications make it impractical to detail the operating conditions. Consult the manufacturer's instructions for the operation of the ICP-MS instrument. Follow the recommendations from the manufacturer to choose the appropriate isotopic masses and parameters to address possible interferences.

8.5.1 Prepare calibration solutions with the elements to be quantified in the test sample using multi-element standard material.

8.5.2 Set up the ICP-MS with all appropriate parameters as recommended by the manufacturer to achieve appropriate detection limits and precision.

8.5.3 Test the samples as recommended by the instrument manufacturer.

9. Calculation

9.1 The calculation, as noted in Eq 1, is usually performed automatically by the instrument software.

$$Ei[\mu g/g] = \frac{Vi \cdot Vfinal}{W} \cdot DF \qquad (1)$$

where:

Ei = element concentration of trace metal i (μg/g sample),
Vi = measured value for element i (μg/cm^3),
W = weight of carbon black sample [g],
$Vfinal$ = end volume of digestion solution [cm^3], and
DF = dilution factor.

10. Report

10.1 Report the following information:

10.1.1 Proper identification of the sample.

10.1.2 A result, for each element, reported to integer ppm, or to the nearest 0.01 % for higher element contents.

11. Precision and Bias

11.1 Precision and bias have not been determined yet.