Designation: G144 – 01 (Reapproved 2014)

Standard Test Method for Determination of Residual Contamination of Materials and Components by Total Carbon Analysis Using a High Temperature Combustion Analyzer[1]

This standard is issued under the fixed designation G144; 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 residual contamination in an aqueous sample by the use of a total carbon (*TC*) analyzer. When used in conjunction with Practice G131 and G136, this procedure may be used to determine the cleanliness of systems, components, and materials requiring a high level of cleanliness, such as oxygen systems. This procedure is applicable for aqueous-based cleaning and sampling methods only.

1.2 This test method is not suitable for the evaluation of particulate contamination, or contaminants that are not soluble in or that do not form an emulsion with water.

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]

D1193 Specification for Reagent Water

D2579 Test Method for Total Organic Carbon in Water (Withdrawn 2002)[3]

F331 Test Method for Nonvolatile Residue of Solvent Extract from Aerospace Components (Using Flash Evaporator)

G121 Practice for Preparation of Contaminated Test Coupons for the Evaluation of Cleaning Agents

G131 Practice for Cleaning of Materials and Components by Ultrasonic Techniques

G136 Practice for Determination of Soluble Residual Contaminants in Materials by Ultrasonic Extraction

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *contaminant (contamination), n*—unwanted molecular and particulate matter that could affect or degrade the performance of the components upon which they reside.

3.1.2 *nonvolatile residue (NVR), n*—molecular and particulate matter remaining following the filtration and controlled evaporation of a liquid containing contaminants.

3.1.3 *Discussion*—In this test method, the *NVR* may be uniformly distributed as in a solution or an emulsion, or in the form of droplets. Molecular contaminants account for most of the *NVR*.

3.1.4 *particle (particulate contaminant), n*— a piece of matter in a solid state with observable length, width, and thickness.

3.1.5 *Discussion*—The size of a particle is usually defined by its greatest dimension and is specified in micrometres.

3.1.6 *molecular contaminant (non-particulate contamination), n*—the molecular contaminant may be in a gaseous, liquid, or solid form.

4. Summary of Test Method

4.1 A test method is described for the quantitative analysis of aqueous samples and may be used in the determination of contamination on parts, components, and materials used in systems requiring a high degree of cleanliness. The residue removed during aqueous cleaning or sampling, using cleaning methods such as Practice G131 and Practice G136, are analyzed using a high-temperature combustion analyzer with a sensitivity of ±0.2 mgC/L (milligrams of carbon per litre). An aqueous sample is injected into the sample port. A stream of oxygen or air carries the sample into the catalytic combustion chamber, which is maintained at a temperature high enough to completely pyrolyze the sample. The sample is combusted in the catalytic combustion chamber and the products are carried by the oxygen or air stream into a nondispersive infrared

[1] This test method is under the jurisdiction of ASTM Committee G04 on Compatibility and Sensitivity of Materials in Oxygen Enriched Atmospheres and is the direct responsibility of Subcommittee G04.01 on Test Methods.

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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.

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

(NDIR) detector where the amount of carbon dioxide in the gas stream is determined. Additional information on the use and operation of carbon analyzers is provided in Test Methods D2579.

4.2 Experience has shown that the bulk of the contaminants are oils and greases; therefore, the samples will typically be emulsions rather than solutions. Thus, proper handling and preparation techniques are necessary in order to obtain good sample homogeneity.

5. Significance and Use

5.1 It is expected that this test method will be suitable for the quantitative determination of total carbon in water that has been used to clean, extract, or sample parts, components, materials, or systems requiring a high degree of cleanliness, that is, oxygen systems.

6. Apparatus

6.1 A total carbon analyzer consists of a high-temperature *TC* analyzer[4] that typically utilizes a syringe injection port to introduce the sample into the analyzer, a furnace containing a high-temperature catalytic combustion tube to oxidize carbon to carbon dioxide, a NDIR detector to quantitatively determine the carbon dioxide, associated tubing to connect the functional analytical modules, and a display and control device. A minimum sensitivity of ±0.2 mgC/L is required.

6.1.1 *Injection Port*—Provides a method for the introduction of the sample into the analyzer.

6.1.2 *High-Temperature Furnace*—The high-temperature furnace maintains the combustion tube at a predetermined value. The combustion tube contains a catalytic bed to oxidize any organic carbon to carbon dioxide.

6.1.3 *NDIR Detector*—The nondispersive infrared detector determines the quantity of carbon dioxide that is eluted from the combustion tube.

6.2 *Syringe*—A sampling syringe for injection of the sample into the *TC* analyzer.

6.3 *Bottle*—Amber borosilicate for storage of the calibration solutions.

6.4 *Parts Pan*—Stainless steel container, typically with a volume between 1 and 4 L, used to contain the parts during cleaning.

7. Reagents

7.1 *Deionized Water,* (reagent water), conforming to Specification D1193, Type II containing less than 0.2 mgC/L. Test Method D2579 provides detailed instructions if it may become necessary to purge dissolved carbon dioxide from the water in order to achieve this level of carbon in the water.

7.2 *Carrier Gas,* high-purity oxygen, >99.990 %, <1 ppm CO and CO_2, <1 ppm total hydrocarbons. Oxygen of higher purity may be used if desired. Air that has a hydrocarbon level less than 1.0 ppm may also be used.

7.3 *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 specification are available.[5] 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.

7.3.1 *Anhydrous Potassium Hydrogen Phthalate*—($KC_8H_5O_4$).

7.3.2 *Concentrated Phosphoric Acid.*

7.3.3 *Concentrated Sulfuric Acid.*

7.3.4 *Concentrated Nitric Acid.*

7.3.5 *Sodium Hydroxide.*

8. Sample Handling

8.1 Sample handling is of critical importance in carbon analysis to avoid contaminating the sample. Good laboratory techniques are imperative due to the natural abundance of carbon in the environment. The following recommendations are provided for sample handling during collection, pretreatment, and analysis.

8.2 All glassware including syringes, should be treated prior to use to remove traces of residual carbon. Typical treatments include sodium hydroxide, hot nitric acid, or hot sulfuric acid. Drain, cool, and rinse with Type II reagent water.

8.3 Use a dedicated syringe for each particular carbon range. When the syringe becomes contaminated, as may be indicated by incomplete wetting of the inner surface, reapply treatment in accordance with 8.2.

9. Preparation of Standard Solutions

9.1 Use Specification D1193, Type II water for the preparation of all standard solutions. The water shall have a *TC* level of less than 0.2 mgC/L.

9.2 Prepare a standard total carbon stock solution. Weigh out 2.126 g of potassium hydrogen phthalate and place into a 100-mL volumetric flask. Add 50 to 75 mL of Type II water to dissolve the chemical. Add about 0.1 mL of concentrated sulfuric or phosphoric acid to adjust the pH below 3, and fill to the 100-mL mark with Type II water. This will provide a solution concentration of 10 000 mgC/L. The following formula may be used to calculate the mgC/L:

$$\text{mgC/L} = \frac{N \times 12.01 \times wt}{MW} \times 10^4 \quad (1)$$

where:

mgC/L = milligrams of carbon per litre of solution,
N = number of carbon atoms per standard (phthalate) molecule,
12.01 = atomic weight of carbon,

[4] Satisfactory equipment is the DC-190 TC Analyzer from Rosemount Analytical Inc., Dohrmann Division, 3240 Scott Blvd., P.O. Box 58007, Santa Clara, CA 95052-8007.

[5] *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.

wt = weight of carbon-containing compound, g, and
MW = molecular weight of the carbon-containing compound.

Store the stock solutions in amber borosilicate bottles with PTFE-lined closures at 4°C.

9.2.1 Replace the solution monthly. Date the solution when prepared or list the expiration date on the label.

9.3 Prepare total carbon working standard solutions from the standard stock solution prepared in 9.2, of 1.0 and 5.0 mgC/L for expected sample concentrations less than 5.0 mgC/L. If sample concentrations are expected to exceed 5.0 mgC/L, a standard solution at least twice the expected concentration shall be prepared. It is recommended that 1 L of solution be prepared for total carbon values of 10 mgC/L and below.

9.3.1 Store the working calibration total carbon standard solutions at 4°C in borosilicate bottles with PTFE-lined closures.

9.3.2 Replace the working calibration solutions weekly. Date the solution when prepared or list the expiration date on the label.

10. Preparation of Apparatus

10.1 Prepare the *TC* analyzer for operation in accordance with the manufacturer's instructions.

NOTE 1—It has been found that many manufacturers of this type of equipment do not specify a high enough temperature to completely pyrolyze the sample to carbon dioxide. Therefore, it is recommended that the minimum operating temperature to effect full pyrolysis be determined for the particular instrument selected for this analysis. One indication of an insufficient combustion temperature is a non-repeatability of values for a calibration solution. Typical temperatures required for the pyrolysis of fluorinated hydrocarbons to carbon dioxide in this type of instrument have been found to be in excess of 800°C.

11. Start-up and Calibration Procedure

11.1 Follow the manufacturer's instructions for start-up.

NOTE 2—Many units may be left in a standby mode overnight. In this case the start-up procedure is usually greatly simplified and operations may be quickly resumed in the morning.

11.2 The *TC* analyzers may usually be calibrated using a one- or two-point procedure. Follow the manufacturer's instructions for calibration using the working standards prepared in 9.3.

11.3 To verify that the instrument is operating properly, perform functional tests using 1.0- and 5.0-mgC/L standards. A minimum of three injections shall be performed for each solution and the results averaged to determine the calibration value.

11.3.1 Determine the blank value for the Type II water and clean parts pan used in the cleaning process and record as TC_b. The blank value should read <1.0 mgC/L. If the value exceeds 1.0 mgC/L, reclean the parts pan and repeat the blank value determination. If the value again exceeds 1.0 mgC/L, fresh reagent water shall be obtained and used for the analysis.

11.3.2 The average value for the 1.0- and 5.0-mgC/L calibration standards should read 0.85–1.15 mgC/L and 4.8–5.2 mgC/L, respectively. If the values for the calibration standards do not fall within the specified ranges, discard and prepare new calibration standards. The standard deviation should not exceed ±0.2 mgC/L.

12. Procedure

12.1 Determine the *TC* content of samples obtained from parts that have been extracted with Type II water in accordance with Practice G131 or Practice G136.

12.1.1 Agitate the parts pan from which the water sample will be withdrawn to obtain as homogeneous a solution or emulsion as possible.

12.1.2 Draw a sample of water from the sampling pan with a syringe.

12.1.3 Inject the sample of water into the *TC* analyzer following the instrument operating instructions and record the *TC* results.

12.1.4 Repeat the analysis two times, and record the results for each injection and the average for the three analyses as TC_S in mgC/L.

12.2 For samples taken from parts for the purpose of cleanliness verification, an *NVR* value may be calculated from the *TC* value. In order to calculate the *NVR*, a sensitivity factor (SF) must be determined. This requires some knowledge of the composition of the contaminant. For use of this technique in a manufacturing facility, the problem is easily resolved because the manufacturer knows the identity of the materials used in the processes, that is, cutting oils, adhesives, solder flux, and so forth. For an independent cleaning facility, the problem becomes much more difficult.

NOTE 3—The contaminant may be a single compound or a mixture of several compounds. The majority of materials used in processes are mixtures and the actual contaminant should be used to determine *SF*.

12.2.1 To determine the *SF* based on the mass of a known contaminant, disperse 1.0 mg of the contaminant in a 500-mL volume of water. Perform the carbon analysis 20 times, average the results, and record as the SF_M. The SF_M may be derived by the following:

$$SF_M = TC/S \quad (2)$$

where:

SF_M = sensitivity factor (mgC/mg of contaminant),
TC = average total carbon value of the sample (mgC/L), and
S = contaminant solution concentration (mg/L).

Many contaminants are not soluble in water. Heating the water and ultrasonic agitation may be required to adequately emulsify the contaminant.

12.2.1.1 Some contaminants are very difficult to emulsify directly. Some success has been achieved by applying a known amount of contaminant to a small, thin, lightweight coupon such as shim stock. Then the coupon is ultrasonically agitated in a known amount of heated water. The coupon is dried and reweighed. The difference in coupon weight is the amount of contaminant extracted into the water. The water sample is analyzed for *TC* and a *SF* can then be calculated based on the known contaminant concentration and the measured *TC*.

12.2.2 If a sample of the known contaminant is not available, but the percentage of each component in the mixture is known, determine the SF_M for each component in the

mixture as described in 12.31. Then multiply the *SF* determined for each component of the mixture by the weight fraction of that component in the mixture. Sum the values and record the sum as the SF_M for the mixture.

12.2.3 If the percentage of each component in the mixture is unknown, estimate the percentage of that component in the mixture and proceed as if the percentage is known.

12.2.4 Another method to determine the SF_M of a mixture with unknown composition is to determine the SF_M of each suspected component and then adjust the SF_M for that component by estimating the probability of that component being in the mixture. Then sum the probability adjusted SF_M's for each component and record the sum as the SF_M for the mixture.

12.2.5 If sufficient quantities of the contaminant are available, a set of contaminated coupons may be prepared in accordance with Practice G121. Verify half of the coupons using a standard solvent cleaning process on the coupons and an aqueous cleaning process on the other half. Determine the NVR_C for the solvent-cleaned coupons using a procedure such as Test Method F331 and sample the reagent water and the water from the aqueous cleaning process to determine TC_b and TC_s. Record the values for the NVR_C, TC_b, and TC_S, respectively.

NOTE 4—This procedure is an indirect method and the *SF* derived is influenced by: 1) the specific solvent selected, 2) the ability of the selected solvent to completely remove the contaminant, and 3) the accuracy of the *NVR* technique.

12.2.5.1 Derive the SF_A based on surface area as follows:

$$SF_A = \{(TC_S - TC_b)V_W\}/\{(NVR_C)A\} \quad (3)$$

where:

SF_A = emperically derived constant, mgC/mg contaminant,
TC_S = average total carbon value of the sample, mgC/L,
TC_b = average carbon value of the blank, mgC/L,
V_W = volume of water in the parts sampling pan, L,
NVR_C = nonvolatile residue, mg contaminant/m^2, and
A = surface area of parts, m^2.

12.2.5.2 Derive the SF_M based on mass as follows:

$$SF_M = \{(TC_S - TC_b)V_W\}/\{(NVR_C)M\} \quad (4)$$

where:

SF_M = emperically derived constant, mgC/mg contaminant,
TC_S = average total carbon value of the sample, mgC/L,
TC_b = average carbon value of the blank, mgC/L,
V_W = volume of water in the parts sampling pan, L,
NVR_C = nonvolatile residue, mg contaminant/g of parts, and
M = weight of the parts, g.

13. Calculation

13.1 Calculate the *NVR* as follows:

$$NVR = \{(TC_S - TC_b)V_W\}/\{(SF)A\} \quad (5)$$

or,

$$NVR = \{(TC_S - TC_b)V_W\}/\{(SF)M\} \quad (6)$$

where:

NVR = nonvolatile residue, mg/m^2 or mg/g,
TC_S = average total carbon value of the sample, mgC/L,
TC_b = average carbon value of the blank, mgC/L,
V_W = volume of water in the parts sampling pan, L,
SF = empirically derived constant from Eq 3, Eq 4, or Eq 5, mgC/mg contaminant,
A = surface area of the parts sampled, m^2, and
M = mass of the parts sampled, g.

14. Report

14.1 Report the following information:

14.1.1 Manufacturer of the carbon analyzer,

14.1.2 Model number of the carbon analyzer,

14.1.3 Identification of the contaminant,

14.1.3.1 Chemical name, composition, or trade name, if known,

14.1.3.2 Manufacturer, if known,

14.1.4 Value of TC_b for the reagent water blank, mgC/L,

14.1.5 Value of TC_S for the sample, mgC/L,

14.1.6 Value of the empirically determined sensitivity factor, *SF*, for the contaminant, mgC/mg contaminant, and

14.1.7 Value of the *NVR*, mg/m^2 or mg/g.

15. Precision and Bias

15.1 *Precision*—The precision of the procedure in this test method is being determined.

15.2 *Bias*—Since there is no accepted reference material for the procedure in this test method, bias can not be determined.

16. Keywords

16.1 cleaning; contaminant; contamination; nonvolatile residue; *NVR*; oxygen systems; sensitivity factor; *TC*; total carbon analysis