



Designation: D8186 – 18

Standard Test Method for Measurement of Impurities in Graphite by Electrothermal Vaporization Inductively Coupled Plasma Optical Emission Spectrometry (ETV-ICP OES)¹

This standard is issued under the fixed designation D8186; 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 measurement of mass fractions of the elements silver (Ag), aluminum (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), bismuth (Bi), calcium (Ca), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), potassium (K), lithium (Li), magnesium (Mg), manganese (Mn), molybdenum (Mo), sodium (Na), nickel (Ni), phosphorus (P), lead (Pb), sulfur (S), antimony (Sb), silicon (Si), tin (Sn), strontium (Sr), titanium (Ti), vanadium (V), tungsten (W), yttrium (Y), zinc (Zn), and zirconium (Zr) in graphite.

1.2 Provided that an appropriate validation procedure is carried out, this test method is also applicable to other carbon materials such as coal, coke, carbon black, graphite-felt, graphite-foil, graphite-foam, and fiber reinforced carbon-carbon composites.

1.3 This test method is applicable to element contents from approximately 0.0001 mg/kg to 1000 mg/kg (0.1 ppmw to 1000 ppmw), depending on element, wavelength, measurement parameters, and sample mass.

1.4 The values stated in SI units are to be regarded as standard. The values given in parentheses after SI units are provided for information only and are not considered standard.

1.5 *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.*

1.6 *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

2.2 *ISO Standards:*³

ISO 5725-2 Accuracy (trueness and precision) of measurement methods and results—Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method

3. Terminology

3.1 *Definitions:*

3.1.1 *ETV, n*—electrothermal vaporization.

3.1.2 *ICP OES, n*—inductively coupled plasma optical emission spectrometry.

4. Summary of Test Method

4.1 The ETV unit consists of an electrically heated graphite tube furnace. Graphite boats which fit into the graphite tube are used for inserting the sample, crushed and milled if necessary, into the furnace. Handling of graphite boats is preferably done using an automated system. One end of the furnace, which is sealed with a movable door, is used for inserting the graphite boats (furnace inlet). The other end of the furnace (furnace outlet) is connected via a tube to the injector tube of the ICP-torch. The graphite tube furnace is heated rapidly to a temperature where evaporation of analyte elements takes place. For complete volatilization of analyte elements, a halogenating reaction gas is added to the argon carrier gas stream. The evaporation products containing the analyte elements are transported as dry aerosol with the argon carrier gas stream from the furnace outlet to the ICP-torch where they are excited to emit optical radiation. The emitted radiation is dispersed and detected by a simultaneous spectrometer. The intensity of radiation of emission lines and background (optional) is

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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 Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

measured with appropriate detectors. The mass fractions of the analyte elements are calculated by comparing the intensities of the element-specific spectral lines of the sample with calibration samples of known analyte content.

4.2 For ICP OES, sample introduction is usually done by nebulization of liquids. In the case of graphite, sample decomposition prior to analysis is required, for example, by ashing, melt-fusion, or acid/pressure-decomposition. These decomposition procedures are time-consuming, and the possibility of introduction of impurities as well as analyte losses represents a serious source of systematic errors. In ETV-ICP OES, sample introduction by nebulization of liquids is replaced by the electrothermal vaporization of solid samples at high temperatures in a graphite tube furnace, thus eliminating the need for wet chemical sample decomposition prior to analysis. In general, ETV-ICP OES provides a linear working range of up to four orders of magnitude. This range can be expanded for the respective elements by selecting emission lines with different sensitivity or variation of sample mass, or both.

4.3 A prerequisite for ETV-ICP OES is an efficient transport of the gaseous products generated in the graphite tube furnace during the heating step to the ICP-torch. This is achieved by a suitable graphite tube design and gas regime in the transition area between the graphite tube and transport tube as shown in Figs. 1 and 2. See also Refs (1-4).⁴ A nozzle-type graphite tube and the use of a bypass-gas in the gap between the graphite tube and transport tube are the key factors for high and reproducible transport efficiencies as well as minimized matrix effects. The temperature of the graphite tube furnace in the evaporation step depends on the analytes to be determined. Release of volatile analytes (such as arsenic, cadmium, potassium, lithium, and sodium) from the graphite matrix starts at 500 °C to 800 °C. To measure all elements listed in 1.1 a temperature of 2600 °C is required.

4.4 By addition of a halogen-containing reaction gas to the carrier gas, the vaporization temperatures of elements are lowered through the formation of volatile halides. In the case of carbide-forming elements, halogenation is a prerequisite to

vaporize these elements. In addition, aerosols formed by pyrolysis of the reaction gas act as condensation nuclei for sample vapors, which have a positive effect on transport efficiency (see Refs (1-3), (5-7)). To measure all elements listed in 1.1, dichlorodifluoromethane (CCl_2F_2) shall be used as reaction gas. Using other reaction gases (for example, CF_4 , CCl_2F_2 , CHF_3 , CHClF_2 , $\text{C}_2\text{H}_2\text{F}_4$, SF_6 , and NF_3) may result in reduced release of some analytes from the graphite matrix.

4.5 The dry aerosol is transported by means of suitable tubing to the injector tube of the plasma torch of the ICP spectrometer where it is excited to emit optical radiation (see Fig. 3).

4.6 A description of possible interferences and their elimination is given in Appendix X2.

5. Significance and Use

5.1 The presence and content of various impurities in graphite are major considerations in determining the suitability of graphite for various applications. This test method provides an alternative means of determining the content of trace impurities in a graphite sample which has considerable advantages compared to classical wet-chemical analysis methods.

5.2 The test method provides a standard procedure to measure impurities in graphite and to assure required graphite specifications.

6. Apparatus

6.1 Laboratory instruments are required as detailed in 6.2 to 6.8. In the case of the spectrometer (6.2) and the ETV system (6.3), the user shall follow the manufacturer's instructions on use of the apparatus.

6.2 *Inductively Coupled Plasma Optical Emission Spectrometer*—A simultaneous method capable of recording transient emission signals, suited to synchronize data acquisition with an ETV heating cycle.

NOTE 1—In ETV-ICP OES, the evaporating sample may cause a significant alteration to the spectral background near the emission lines, which increases the measurement uncertainty. This effect can be reduced if the spectrometer is capable of measuring the intensity of emission lines and the intensity of spectral background close to the emission lines

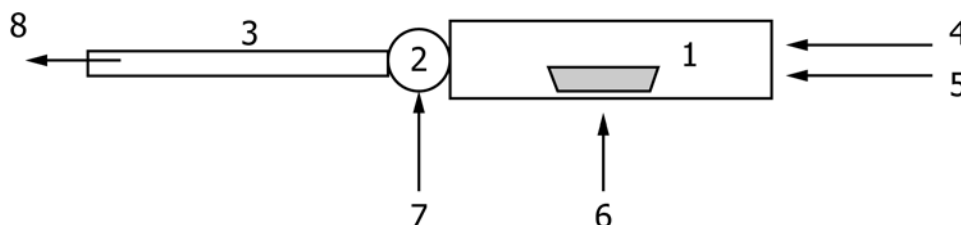


FIG. 1 ETV Unit: Schematic Design of Gas Flows

Key:

- 1 Graphite tube with graphite boat and sample
- 2 Transition area between graphite tube and transport tube
- 3 Transport tube
- 4 Carrier gas (argon)
- 5 Reaction gas (CCl_2F_2)
- 6 Furnace shield gas (argon)
- 7 Bypass gas (argon)
- 8 Dry aerosol to injector tube of plasma torch

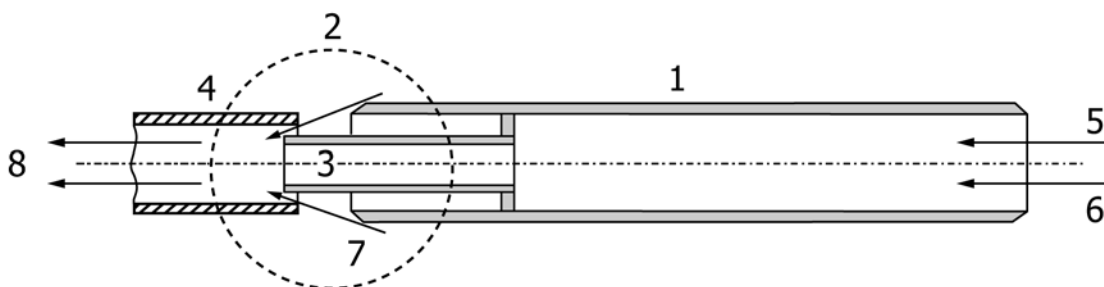


FIG. 2 ETV Unit: Schematic Design of Graphite Tube and Transition Area

- Key:
- 1 Graphite tube
 - 2 Transition area
 - 3 Nozzle of graphite tube
 - 4 Transition tube (alumina)
 - 5 Carrier gas (argon)
 - 6 Reaction gas (CCl_2F_2)
 - 7 Bypass gas (argon)
 - 8 Gas-mixture and dry sample aerosol to injector tube of plasma torch

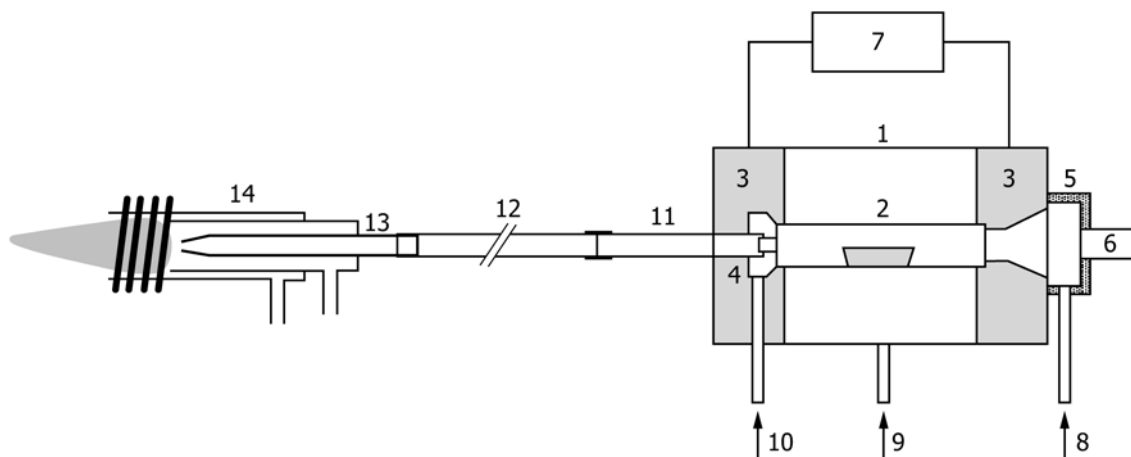


FIG. 3 Schematic Design of ETV Unit and Coupling to ICP

- Key:
- 1 Graphite tube furnace
 - 2 Graphite tube with graphite boat
 - 3 Graphite contacts
 - 4 Transition area
 - 5 Furnace inlet with movable door
 - 6 Pyrometer for online temperature measurement
 - 7 Electrical power supply
 - 8 Carrier gas (argon) and reaction gas (CCl_2F_2)
 - 9 Furnace shield gas (argon)
 - 10 Bypass gas (argon)
 - 11 Transition tube (alumina)
 - 12 Tubing to injector tube of ICP torch
 - 13 Injector tube of ICP torch
 - 14 ICP torch

simultaneously. For method development, it is beneficial if the spectrometer is capable of recording emission signal intensities versus time (so-called “time-scan”).

6.3 Electrothermal Vaporization System—With an electrically heated graphite tube furnace, graphite boats, reproducible setting and continuous control of temperatures up to 2600 °C (tolerance ± 50 °C), programmable temperature versus time runs, controlled gas flows (preferably mass-flow controlled), graphite tube design and transition area between graphite tube and transport tube optimized in terms of dry aerosol formation

and high transport efficiency, heat resistant tubing (up to 150 °C) to connect the ETV system with the ICP-torch, interface for synchronizing the ETV system with the ICP spectrometer.

NOTE 2—Reproducibility of analysis results can be improved using an automated handling system for the graphite boats (autosampler). An autosampler also increases sample throughput and saves working time.

6.4 Balance—Capable of weighing to the nearest 0.01 mg.

6.5 Tweezers.