



Standard Practice for Practice for Sample Decomposition Using Microwave Heating (With or Without Prior Ashing) for Atomic Spectroscopic Elemental Determination in Petroleum Products and Lubricants¹

This standard is issued under the fixed designation D7876; 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 practice covers the procedure for use of microwave radiation for sample decomposition prior to elemental determination by atomic spectroscopy.

1.1.1 Although this practice is based on the use of inductively coupled plasma atomic emission spectrometry (ICP-AES) and atomic absorption spectrometry (AAS) as the primary measurement techniques, other atomic spectrometric techniques may be used if lower detection limits are required and the analytical performance criteria are achieved.

1.2 This practice is applicable to both petroleum products and lubricants such as greases, additives, lubricating oils, gasolines, and diesels.

1.3 Although not a part of Committee D02's jurisdiction, this practice is also applicable to other fossil fuel products such as coal, fly ash, coal ash, coke, and oil shale.

1.3.1 Some examples of actual use of microwave heating for elemental analysis of fossil fuel products and other materials are given in [Table 1](#).

1.3.2 Some additional examples of ASTM methods for microwave assisted analysis in the non-fossil fuels area are included in [Appendix XI](#).

1.4 During the sample dissolution, the samples may be decomposed with a variety of acid mixture(s). It is beyond the scope of this practice to specify appropriate acid mixtures for all possible combinations of elements present in all types of samples. But if the dissolution results in any visible insoluble material, this practice may not be applicable for the type of sample being analyzed, assuming the insoluble material contains some of the analytes of interest.

1.5 It is possible that this microwave-assisted decomposition procedure may lead to a loss of "volatile" elements such as

arsenic, boron, chromium, mercury, antimony, selenium, and/or tin from the samples. Chemical species of the elements is also a concern in such dissolutions since some species may not be digested and have a different sample introduction efficiency.

1.6 A reference material or suitable NIST Standard Reference Material should be used to confirm the recovery of analytes. If these are not available, the sample should be spiked with a known concentration of analyte prior to microwave digestion.

1.7 Additional information on sample preparation procedures for elemental analysis of petroleum products and lubricants can be found in Practice [D7455](#).

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

1.9 *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.* Specific warning statements are given in Sections [6](#) and [7](#).

2. Referenced Documents

2.1 ASTM Standards:²

[C1234 Practice for Preparation of Oils and Oily Waste Samples by High-Pressure, High-Temperature Digestion for Trace Element Determinations](#)

[C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis](#)

[C1463 Practices for Dissolving Glass Containing Radioactive and Mixed Waste for Chemical and Radiochemical Analysis](#)

[D482 Test Method for Ash from Petroleum Products](#)

¹ This practice is under the jurisdiction of ASTM Committee [D02](#) on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee [D02.03](#) on Elemental Analysis.

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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.

TABLE 1 Referenced Examples of Microwave Heating for Dissolution of Fossil Fuel and other Samples

Material	Element(s) Determined	Measurement Technique	Reference ^A
Biological Materials	Multiple	AAS and NAA	Abu Samra et al (1)
Biological Materials	Multiple	AAS and NAA	Barrett et al (2)
			West et al (3)
Geological Materials	Multiple		Matthes et al (4)
Oil Shales	Multiple	ICP-AES	Nadkarni (5)
Coal and Fly Ash	Multiple	ICP-AES	Nadkarni (5)
Plant and Grain Standards	Multiple	ICP-MS	Feng et al (6)
Greases	Multiple	ICP-AES	Fox (7); Nadkarni (8)
Petroleum Products	Multiple	ICP-AES	Hwang et al (9)
Crude Oil	Multiple	ICP-MS	Xie et al (10)
Residual Fuel Oil	Multiple	ICP-MS	Wondimu et al (11)
Oils	Lanthanides and Platinum Group Metals	ICP-MS	Woodland et al (12)
		AAS; ICP-AES	Kingston and Jassie (13)
		AAS; ICP-AES	Kingston and Haswell (14)
Soils and Sediments	Lanthanides	ICP-MS	Ivanova et al (15)

^A The boldface numbers in parentheses refer to the list of references at the end of this standard.

D874 Test Method for Sulfated Ash from Lubricating Oils and Additives

D1193 Specification for Reagent Water

D1506 Test Methods for Carbon Black—Ash Content

D2216 Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products

D4309 Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Metals in Water

D4628 Test Method for Analysis of Barium, Calcium, Magnesium, and Zinc in Unused Lubricating Oils by Atomic Absorption Spectrometry

D4643 Test Method for Determination of Water (Moisture) Content of Soil by Microwave Oven Heating

D4951 Test Method for Determination of Additive Elements in Lubricating Oils by Inductively Coupled Plasma Atomic Emission Spectrometry

D5185 Test Method for Determination of Additive Elements, Wear Metals, and Contaminants in Used Lubricating Oils and Determination of Selected Elements in Base Oils by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)

D5258 Practice for Acid-Extraction of Elements from Sediments Using Closed Vessel Microwave Heating

D5513 Practice for Microwave Digestion of Industrial Furnace Feedstreams and Waste for Trace Element Analysis

D5765 Practice for Solvent Extraction of Total Petroleum Hydrocarbons from Soils and Sediments Using Closed Vessel Microwave Heating

D5862 Test Method for Evaluation of Engine Oils in Two-Stroke Cycle Turbo-Supercharged 6V92TA Diesel Engine (Withdrawn 2009)³

D6010 Practice for Closed Vessel Microwave Solvent Extraction of Organic Compounds from Solid Matrices

D6792 Practice for Quality System in Petroleum Products and Lubricants Testing Laboratories

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

D7303 Test Method for Determination of Metals in Lubricating Greases by Inductively Coupled Plasma Atomic Emission Spectrometry

D7455 Practice for Sample Preparation of Petroleum and Lubricant Products for Elemental Analysis

D7740 Practice for Optimization, Calibration, and Validation of Atomic Absorption Spectrometry for Metal Analysis of Petroleum Products and Lubricants

E1358 Test Method for Determination of Moisture Content of Particulate Wood Fuels Using a Microwave Oven

E1645 Practice for Preparation of Dried Paint Samples by Hotplate or Microwave Digestion for Subsequent Lead Analysis

2.2 Other documents:

CFR 1030.10 Radiological Health

FCC Rule Part 18 Labelling Guidelines, Labelling, Information to User, Information in Manual, User Manual

3. Terminology

3.1 Definitions:

3.1.1 *AAS, n*—atomic absorption spectrometry, an analytical technique for measuring metal content of solutions, based on a combination of flame source, hollow cathode lamp, photomultiplier, and a readout device. **D7740**

3.1.2 *additive, n*—a material added to another, usually in small quantities, to impart or enhance desirable properties or to suppress undesirable properties. **D5862**

3.1.3 *blank, n*—solution which is similar in composition and contents to the sample solution but does not contain the analyte being measured. **D7740**

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

3.1.4 *certified reference material, n*—a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by a traceable certificate or other documentation which is issued by a certifying body. **D6792**

3.1.5 *dilution factor, n*—ratio of the sample weight of the aliquot taken to the final diluted volume of the solution.

3.1.5.1 *Discussion*—The dilution factor is used to multiply the observed reading and obtain the actual concentration of the analyte in the original sample. **D7740**

3.1.6 *ICP-AES, n*—inductively coupled plasma atomic emission spectrometry, a high temperature discharge generated by passing an ionizable gas through a magnetic field induced by a radio frequency coil surrounding the tubes that carry gas. The light emitted by excited atoms by this process is measured at fixed wavelengths specific to elements of interest and converted to their concentrations in a sample.

3.1.7 *reference material (RM), n*—a material with accepted reference value(s), accompanied by an uncertainty at a stated level of confidence for desired properties, which may be used for calibration or quality control purposes in the laboratory.

3.1.7.1 *Discussion*—Sometimes these may be prepared “in-house” provided the reference values are established using accepted standard procedures. **D6792**

3.1.8 *standard reference material (SRM), n*—trademark for reference materials certified by National Institute of Standards and Technology. **D7740**

4. Summary of Practice

4.1 A weighed portion of the sample is subjected to alternate means of sample dissolution which may include (optional) sulfated ashing in a muffle furnace followed by closed or open vessel microwave digestion in acid(s). Ultimately, these diluted acid solutions are analyzed using AAS or ICP-AES. By comparing absorbance or emission intensities of elements in the test specimen with those measured of the calibration standards, the concentrations of elements in the test specimen can be calculated.

4.1.1 The final elemental determinations can also be done using ICP-MS; cold vapor and hydride generation AFS/AAS can be used for mercury and hydride forming elements; however, there is no standard ASTM procedure for such work at present.

4.2 Optimal conditions for microwave digestion depend on sample weight, composition, volume of digestion acid reagents, and the microwave system used.

5. Significance and Use

5.1 Often it is necessary to dissolve the sample, particularly if it is a solid, before atomic spectroscopic measurements. It is advantageous to use a microwave oven for dissolution of such samples since it is a far more rapid way of dissolving the samples instead of using the traditional procedures of dissolving the samples in acid solutions using a pressure decomposition vessel, or other means.

5.2 The advantage of microwave dissolution includes faster digestion that results from the high temperature and pressure

attained inside the sealed containers. The use of closed vessels also makes it possible to eliminate uncontrolled trace element losses of volatile species that are present in a sample or that are formed during sample dissolution. Volatile elements arsenic, boron, chromium, mercury, antimony, selenium, and tin may be lost with some open vessel acid dissolution procedures. Another advantage of microwave aided dissolution is to have better control of potential contamination in blank as compared to open vessel procedures. This is due to less contamination from laboratory environment, unclean containers, and smaller quantity of reagents used (9).

5.3 Because of the differences among various makes and models of satisfactory devices, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular device.

5.4 *Mechanism of Microwave Heating*—Microwaves have the capability to heat one material much more rapidly than another since materials vary greatly in their ability to absorb microwaves depending upon their polarities. Microwave oven is acting as a source of intense energy to rapidly heat the sample. However, a chemical reaction is still necessary to complete the dissolution of the sample into acid mixtures. Microwave heating is internal as well as external as opposed to the conventional heating which is only external. Better contact between the sample particles and the acids is the key to rapid dissolution. Thus, heavy nonporous materials such as fuel oils or coke are not as efficiently dissolved by microwave heating. Local internal heating taking place on individual particles can result in the rupture of the particles, thus exposing a fresh surface to the reagent contact. Heated dielectric liquids (water/acid) in contact with the dielectric particles generate heat orders of magnitude above the surface of a particle. This can create large thermal convection currents which can agitate and sweep away the stagnant surface layers of dissolved solution and thus, expose fresh surface to fresh solution. Simple microwave heating alone, however, will not break the chemical bonds, since the proton energy is less than the strength of the chemical bond (5).

5.4.1 In the electromagnetic irradiation zone, the combination of the acid solution and the electromagnetic radiation results in near complete dissolution of the inorganic constituents in the carbonaceous solids. Evidently, the electromagnetic energy promotes the reaction of the acid with the inorganic constituents thereby facilitating the dissolution of these constituents without destroying any of the carbonaceous material. It is believed that the electromagnetic radiation serves as a source of intense energy which rapidly heats the acid solution and the internal as well as the external portions of the individual particles in the slurry. This rapid and intense internal heating either facilitates the diffusion processes of the inorganic constituents in solution or ruptures the individual particles thereby exposing additional inorganic constituents to the reactive acid. The heat generated in the aqueous liquid itself will vary at different points around the liquid-solid interface and this may create large thermal convection currents which can agitate and sweep away the spent acid solution, making