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## Standard Practice for Preparation of Oils and Oily Waste Samples by High- Pressure, High-Temperature Digestion for Trace Element Determinations<sup>1</sup>

This standard is issued under the fixed designation C 1234; 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 approval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This practice describes a high-pressure, high-temperature digestion technique using the high-pressure asher (HPA) for preparation of oils and oily waste specimens for determination of up to 28 different elements by inductively coupled plasma-atomic emission spectroscopy (ICP-AES), cold-vapor atomic absorption spectroscopy (CVAAS), and graphite furnace atomic absorption spectroscopy (GFAAS), inductively coupled plasma-mass spectrometry (ICPMS), and radiochemical methods. Oily and high-percentage organic waste streams from nuclear and non-nuclear manufacturing processes can be successfully prepared for trace element determinations by ICP-AES, CVAAS, and GFAAS. This practice is applicable to the determination of total trace elements in these mixed wastes. Specimens prepared by this practice can be used to characterize organic mixed waste streams received by hazardous waste treatment incinerators and for total element characterization of the waste streams.

1.2 This practice is applicable only to organic waste streams that contain radioactivity levels that do not require special personnel or environmental protection from radioactivity or other acute hazards.

1.3 A list of elements determined in oily waste streams is found in Table 1.

1.4 This test practice has been used successfully to completely digest a large variety of oils and oily mixed waste streams from nuclear processing facilities. While the practice has been used to report data on up to 28 trace elements, its success should not be expected for all analytes in every specimen. The overall nature of these oily wastes tends to be heterogeneous that can affect the results. Homogeneity of the prepared sample is critical to the precision and quality of the results.

1.5 This practice is designed to be applicable to samples whose preparation practices are not defined, or not suitable, by

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**TABLE 1 List of Elements and Applicable Lower Concentration Ranges**

Element	Lower Reportable Limit, <sup>4</sup> $\mu\text{g/g}$	Analysis Method
Aluminum	3.3	ICP-AES
Antimony	8.3	ICP-AES or GFAAS
Arsenic	8.3	ICP-AES or GFAAS
Barium	0.17	ICP-AES
Beryllium	0.05	ICP-AES
Boron	0.67	ICP-AES
Cadmium	0.50	ICP-AES or GFAAS
Calcium	0.67	ICP-AES
Chromium	1.7	ICP-AES
Cobalt	0.83	ICP-AES
Copper	0.67	ICP-AES
Iron	0.67	ICP-AES
Lead	8.3	ICP-AES or GFAAS
Lithium	0.67	ICP-AES
Magnesium	0.08	ICP-AES
Manganese	0.17	ICP-AES
Mercury	0.03	CVAAS
Nickel	1.7	ICP-AES
Potassium	100	ICP-AES
Selenium	8.3	ICP-AES or GFAAS
Silver	1.0	ICP-AES
Sodium	3.3	ICP-AES
Strontium	0.07	ICP-AES
Thallium	1.7	GFAAS
Titanium	0.50	ICP-AES
Vanadium	0.83	ICP-AES
Zinc	0.17	ICP-AES
Zirconium	0.83	ICP-AES

<sup>4</sup> Lower reportable limits are based on a 0.3-g sample diluted to a final volume of 50 mL. These limits should only be used as a guide. Actual values are instrument and sample dependent.

other regulatory procedures or requirements, such as the U.S. Environmental Protection Agency (EPA) SW-846 and EPA-600 4-79-020 documents. This digestion practice is designed to provide a high level of accuracy and precision, but does not replace or override any regulatory requirements for sample preparation.

1.6 This practice uses hazardous materials, operations, and equipment at high pressure (90–110 bars, 89–108 atm, or 1305–1595 lb/in.<sup>2</sup>) and high temperatures, up to 320°C, and therefore poses significant hazards if not operated properly. *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility*

TABLE 2 HPA Temperature Program for Oils and Oily Waste Samples

Phase	Starting Temperature, °C	Time, min	Ending Temperature, °C
1	100	30	125
2	125	60	300
3	300	60	300
4	25	30	25
5	0	0	0

of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Specific hazard statements are given in Sections 10 and 11.

## 2. Referenced Documents

### 2.1 ASTM Standards:

D 1193 Specification for Reagent Water<sup>2</sup>

E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods<sup>3</sup>

### 2.2 US EPA Standards:

Methods for Chemical Analysis of Water and Wastes, 600/4-79-020, 1983<sup>4</sup>

Test Methods for Evaluating Solid Waste, SW-846, 3rd Ed., 1986<sup>4</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 *heating block*—aluminum block used to hold samples inside the HPA autoclave/pressure chamber.

3.1.2 *HPA-TC controller*—computer interface between HPA autoclave and an IBM-compatible computer.

3.1.3 *pressure chamber*—chamber within the HPA autoclave where heating block filled with samples is placed. The chamber is designed to hold pressures up to 200 bar (197 atm or 2900 lb/in.<sup>2</sup>) and temperatures up to 320°C.

3.1.4 *safety lid vent stack*—top plate and cylinder that covers the autoclave pressure chamber.

3.1.5 *sample vessel*—sample container, constructed of quartz or glassy carbon, designed for use in the HPA.

3.1.6 *temperature program*—software program which controls the temperature ramping of the HPA during the run. The program used for preparation of oil samples is shown in Table 2.

## 4. Summary of the Practice

4.1 Oil or oily waste specimens are digested in nitric and hydrochloric acids using HPA high-pressure, high-temperature equipment. Prepared specimens of 0.2 to 0.7 g will provide enough solution for analysis by CVAAS, ICP-AES, and GFAAS for up to 28 elements.

## 5. Significance and Use

5.1 This practice is useful for preparation of difficult-to-digest, primarily oils and oily wastes, specimens for trace element determinations of up to 28 elements by atomic

absorption or plasma emission techniques. Specimen preparation by high-pressure ashing is primarily applicable to specimens whose preparation by EPA SW-846 protocols is either not applicable or not defined. This sample preparation practice is applicable for the trace element characterization of mixed oily wastes for use by waste treatment facilities such as incinerators or waste stabilization facilities.

## 6. Interferences

6.1 Preparation of samples for trace element determinations is subject to matrix and chemical interferences. Although the HPA practice is designed to totally digest most matrices, there are some matrix types that are not applicable to this practice, for example, highly reactive substances (explosives), extremely flammable materials, and some silicone-based lubricants.

## 7. Apparatus

7.1 *HPA High Pressure Asher*<sup>5</sup>—High-pressure, high-temperature autoclave under computer control allowing complete digestion of difficult specimens using mineral acids. The system includes:

7.1.1 Compatible computer with hard drive and with one open RS-232C serial interface.

7.1.2 HPA-TC temperature controller—this device provides the interface between the HPA autoclave and the computer by means of RS-232C serial interface.

7.1.3 HPA autoclave unit.

7.1.4 HPA sample vessels, appropriate size and construction for specimen type and mineral acid used.

7.2 *Ultrasonic Homogenizer*—Specimen homogenizer using ultrasonic disruption tip to homogenize specimens that cannot be mixed by hand.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Chemicals used in the preparation of spiking standards must be of ultra purity grade. Chemicals and reagents used in the preparation practice must conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.<sup>6</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination.

8.2 *Reagent Water*—References to water shall be understood to mean reagent water as defined by Type 1 of Specification D 1193.

8.3 *Nitric Acid (sp gr 1.42)*—Ultra pure concentrated nitric acid (HNO<sub>3</sub>).

8.4 *Hydrochloric Acid (sp gr 1.19)*—Ultra pure concentrated hydrochloric acid (HCl).

<sup>5</sup> High-pressure ashing equipment manufactured by Anton Paar K. G., Graz, Austria has been found to be satisfactory for this procedure.

<sup>6</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

<sup>2</sup> Annual Book of ASTM Standards, Vol 11.01.

<sup>3</sup> Annual Book of ASTM Standards, Vol 14.02.

<sup>4</sup> Available from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

8.5 *Hydrofluoric Acid (sp gr 0.988)*—Ultra pure concentrated hydrofluoric acid (HF).

8.6 *Matrix Spiking Standards*—Multielement standards used for matrix spiking shall be of sufficient purity and accuracy and, where possible, traceable to accepted nationally known standards (that is, National Institute of Standards and Technology (NIST) or EPA). Spiking standards used should yield spiked specimens with concentrations between 0.5 to 2 mg/L for most elements.

## 9. Sample Preparation

9.1 Homogeneous specimens are a requirement if suitable analytical precision is expected. Most oils and oily wastes require additional steps to provide homogeneous specimens for preparation. If the sample is visibly clear or can be shaken to provide a homogeneous specimen, no further pretreatment is necessary.

9.2 Liquid or aqueous specimens that are cloudy or contain visible sediment or precipitates may require an ultrasonic bath to resuspend settled material or maintain a homogeneous specimen for preparation. The process of ultrasonic mixing will generate heat, and warm the sample above ambient temperature. A consideration of the original sample must be made as to the effect of ultrasonification on the sample. A sample with a low boiling point, such as freon, may not be applicable to ultrasonic mixing. Ultrasonification between 1 to 5 min is effective for liquid or aqueous samples.

9.3 It is difficult to obtain homogeneous specimens for preparation from multi-phase liquids, oils, oily wastes, or samples with large amounts of solid matter. For these sample types, an ultrasonic sonifier is very useful in providing a homogeneous specimen. The sonifier uses high-frequency electrical energy transmitted through a converter to vibrate a metal horn tip that is immersed in the sample. The vibration of the horn tip causes cavitation of medium that causes the intense agitation of the medium leading to very stable emulsions to be formed, even between polar and non-polar liquids.

9.3.1 The sonification process will generate heat, and the specimen should be checked during the process. Specimen homogenization is determined by visual observation and is normally complete within 10 to 60 s. If heat generation in the sample becomes a problem, determined by the temperature rise in the specimen, then the homogenization should be judged complete when the sample temperature rises to this level, as determined on a specimen by specimen basis. Process and observe each sample individually to obtain the best, most representative results. Specimens with low flash points are not recommended for homogenization by this method.

9.3.2 Process the specimen immediately to maintain its homogeneity.

## 10. Procedure

10.1 Weigh 0.2 to 0.7 g of homogeneous sample into a clean HPA vessel. The sample mass necessary for the HPA is matrix dependent, that is, organic or inorganic content, and samples up to 2 g can be prepared. Sample sizes of 0.2 to 0.7 g are successful for highly organic specimens. The organic component of the specimen will have a direct effect on the digestion in the HPA; the more organic a specimen the more internal

pressure may be generated. Due to the closed vessel HPA technique, the possibility of a specimen venting during the HPA digestion is proportional to its mass.

10.2 Within a preparation batch, with the number of specimens defined by the laboratory, the following quality control samples should be included; a reagent blank containing all reagents used in the procedure, a matrix duplicate specimen for assessing precision, and a matrix spiked specimen for assessing method accuracy. A batch size of ten specimens has been successful for HPA digestion performed on oily waste samples.

10.3 Exercise extreme caution when handling specimens during the pressure decomposition process, as spontaneous violent reactions may occur under adverse conditions. The safety design features of the HPA equipment allow for sample explosive reactions to occur inside the pressure chamber without adverse effects on the equipment or its operators. A tantalum rupture disk will blow out to relieve the pressure if the internal pressure of the sealed chamber should rise above 200 bars (197 atm or 2900 lb/in.<sup>2</sup>).

**NOTE 1—Caution:** Adequate laboratory facilities, such as fume hoods and controlled ventilation, along with normal safe laboratory techniques, must be used in this procedure. Due to the rupture disk feature, the HPA equipment should always be operated in a fume hood.

10.4 Place sample vessels in the fume hood and add 5 mL concentrated HNO<sub>3</sub> and 2.5 mL HCl. The inclusion of HCl is necessary to solubilize any iron oxyhydroxides which may be present in the specimen or digestate and to yield quantitative recovery of silver and antimony.

10.4.1 Hydrofluoric acid should be used if siliceous materials are being prepared and must be used only in glassy carbon vessels.

**NOTE 2—Caution:** Due to the tendency of hydrofluoric acid to cause severe skin and tissue damage, extreme caution must be exercised when HF is used or may be present.

10.5 Place a layer of 1 in. polytetrafluoroethylene (PTFE) tape over the top of the sample vessel. Check to be sure the surface is smooth and free of ripples. Pierce the tape in the center to provide for pressure equilibration.

**NOTE 3—**Refer to manufacturer's operating manual for high pressure Asher vessel details.

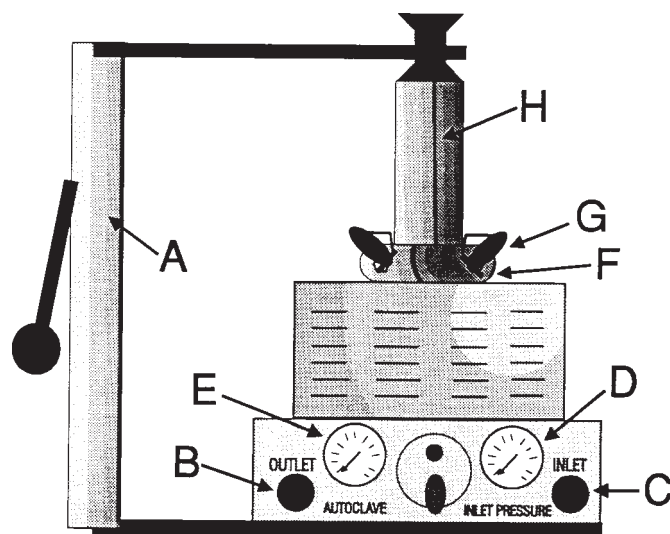
10.6 Place lid on the top of the PTFE tape. Secure the lid to vessel by wrapping PTFE tape around the lid assembly. Two to three windings should suffice to provide for a leak-free seal.

10.7 Place the appropriate heating block into the HPA pressure chamber: (a) 7-position block for 50-mL quartz vessels, (b) 5-position block for 90-mL quartz vessels, (c) 5-position block for 90-mL quartz vessels, Type B, (Note 4), (d) 7-position block for glassy carbon vessels.

**NOTE 4—**The Type B block is used for most oily waste specimens prepared using 90-mL vessels. The "B" block design is a cut-out block that allows for improved distillation of the specimen during decomposition. Only the lower portion of the sample is in contact with this heating block.

10.8 Place the vessels into the heating block. Refer to Fig. 1 for a diagram of the HPA equipment.

10.9 Seal the autoclave pressure chamber with the safety lid vent stack using a hydraulic stack lifter.



- A—Stack lifter (shown in the engaged position)
- B—Autoclave exhaust valve
- C—Pressure regulator valve
- D—Cylinder tank pressure gauge
- E—Autoclave pressure gauge
- F—Retainer rings (front/back)
- G—Fail-safe safety vent valves
- H—Vent stack

**FIG. 1 Diagram of HPA Equipment**

10.10 Close the fail-safe valves on the safety lid vent stack and pressurize the autoclave chamber with an inert gas, argon or nitrogen, between 95 and 110 bars.

10.11 Initialize the computer and HPA-TC unit.

NOTE 5—A computer meeting the manufacturer's specification when loaded with the supplied software performs all necessary Asher control.

10.12 Load the HPA temperature program and initialize run.

NOTE 6—HPA temperature programs are generated by the operator and are stored on the computer hard disk or floppy disk for retrieval. The program shown in Table 2 has been successful for oily waste samples.

NOTE 7—The program shown in Table 2 is provided as a reference or starting point for the HPA preparation. The HPA temperature programs may need development for particular sample types, based on matrix or elemental recovery requirements.

10.13 Allow the HPA to cool following the run before removing digested specimens.

10.14 Depressurize the autoclave chamber by exhausting the pressure slowly through the HPA exhaust valve, over a

period of 3–6 min. Keep hands and arms away from the vent stack during depressurization. The depressurization process should be done slowly so the digested specimens adjust to the pressure change and do not boil or vent.

NOTE 8—**Caution:** Never open the HPA autoclave while it is under pressure. The safety vent stack fail-safe valves should preclude this from occurring; however, the extreme safety risk of opening a pressurized autoclave must be addressed.

10.15 Before proceeding, confirm and double check that the pressure chamber is at ambient pressure. Check the pressure gauges on the front of the HPA and pressure channel on the HPA-TC unit. Check the vent stack to decide if it is cool by carefully touching with hands.

10.16 Open the autoclave by opening the pressure fail-safe valves on the safety lid vent stack and the ring retainer bolts.

10.17 Remove the safety lid vent stack and remove the digested specimens. Keep the digested specimens inside a fume hood due to the slow degassing of nitrous oxides from the digested samples. Specimens may have a blue color due to the presence of dissolved nitrous oxides. A clear solution is obtained when specimens have completely degassed or when they are diluted to volume.

10.18 Transfer the specimens to a clean sample container, and dilute to 50 mL using reagent water. The final solution contains 10 % HNO<sub>3</sub> and 5 % HCl.

## 11. Precision and Bias

11.1 Developmental tests using spiked matrices have shown accuracy to be within 25 % of the spiked level at routine instrumental reporting levels for oil matrices. Analytical data useful in establishing procedural precision and bias may not be obtainable for this practice, by the fact that it is a preparation practice and thus produces no analytical data directly. Method developmental testing using spiked oily waste specimens have shown accuracy to be within ±25 % of the spiked concentration, 0.5 to 2.0 mg/L, for these matrices. This practice is a general preparation practice for difficult matrices and is not specific for any element(s). Specific analytical procedures can assess precision and bias (see Practice E 177).

## 12. Keywords

12.1 high-pressure ashing; oily waste; sample preparation; trace metals; atomic spectroscopy

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