



Designation: D7482 – 17

Standard Practice for Sampling, Storage, and Handling of Hydrocarbons for Mercury Analysis¹

This standard is issued under the fixed designation D7482; 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 types of and preparation of containers found most suitable for the handling of hydrocarbon samples for the determination of total mercury.

1.2 This practice was developed for sampling streams where the mercury speciation is predominantly Hg(0) present as a mixture of dissolved Hg(0) atoms, adsorbed Hg(0) on particulates (for example, carbonaceous or mineral fines and Fe₂O₃) and suspended droplets of metallic mercury.

1.3 The presence of suspended droplets of metallic mercury (often called “colloidal” mercury, since the droplet size can be very small) can make obtaining a representative sample very difficult for a variety of reasons (for example, non-isokinetic sampling of the liquid can result in over- or under-collection of suspended droplets and collection of mercury that has accumulated in dense larger drops and pools on the bottom of piping and in sample taps). Pay strict attention to the detailed procedure (Section 7) to ensure representative samples are collected.

1.4 When representative test portions are collected and analyzed in accordance with acceptable procedures, the total mercury is representative of concentrations in the sample.

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 **Warning**—Mercury has been designated by EPA and many state agencies as a hazardous material that can cause central nervous system, kidney, and liver damage. Mercury, or its vapor, may be hazardous to health and corrosive to materials. Caution should be taken when handling mercury and mercury-containing products. See the applicable product Material Safety Data Sheet (MSDS) for details and EPA’s website (<http://www.epa.gov/mercury/faq.htm>) for additional informa-

tion. Users should be aware that selling mercury or mercury-containing products, or both, in your state may be prohibited by state law.

1.7 *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.*

1.8 *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

[D4175 Terminology Relating to Petroleum Products, Liquid Fuels, and Lubricants](#)

[D7622 Test Method for Total Mercury in Crude Oil Using Combustion and Direct Cold Vapor Atomic Absorption Method with Zeeman Background Correction](#)

[D7623 Test Method for Total Mercury in Crude Oil Using Combustion-Gold Amalgamation and Cold Vapor Atomic Absorption Method](#)

2.2 *EPA Standard:*³

[EPA Method 1669 Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels; July 1996; US Environmental Protection Agency](#)

3. Terminology

3.1 *Definitions*—For definitions of terms used in this standard, refer to Terminology [D4175](#).

3.2 *Abbreviations:*

3.2.1 *VOA*—Volatile Organic Analysis

¹ This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, 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.

³ Available from United States Environmental Protection Agency (EPA), Ariel Rios Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460 (www.epa.gov).

*A Summary of Changes section appears at the end of this standard

4. Summary of Practice

4.1 This practice describes the sampling, storage, transport, and handling of hydrocarbon samples used for determining mercury, and the precautions that need to be taken to prevent sample contamination and loss of analyte.

5. Significance and Use

5.1 This practice is intended for use in sampling liquid hydrocarbons including crude oils, condensates, refinery process intermediates, and refined products. Generally these samples are expected to contain mercury from the parts per billion (10^{-9} mass) to parts per million (10^{-6} mass) range.

5.2 This practice is not intended for use when sampling aqueous systems where the concentrations of mercury are often in the parts per trillion (10^{-12} mass) range. These samples are often better addressed by using the rigorously clean techniques from the EPA Method 1669 “clean hands, dirty hands” sampling procedures.

5.3 This practice is not intended for use for liquefied samples, for which special containers may be required for pressurized samples.

5.4 This practice is only suitable for stabilized samples which remain 100 % liquid at ambient conditions. For samples that on depressurization lose some of the light hydrocarbon ends it is important to note that elemental mercury may be lost during sampling. Sampling modules which inject unstabilized liquid hydrocarbons close to process conditions directly to the mercury analyzer can be used to overcome this issue.

5.5 Based on this practice, two Test Methods ([D7622](#) and [D7623](#)) are available for determination of mercury in crude oil, based on cold vapor atomic absorption technique.

5.6 In some refined streams and in tank samples free water may be present. Process streams that are water saturated may condense water as the sample cools from process temperature to ambient temperature. Ionic mercury species are water soluble and these water droplets may contain mercury or adsorb mercury over time.

5.7 The presence of mercury during crude oil production, transport, and refining can be an environmental and industrial hygiene concern.

6. Apparatus

6.1 *Clear or Amber Borosilicate Glass*, 40 mL or less in volume; pre-cleaned by acid-washing; with PTFE (polytetrafluoroethylene)-lined septum caps. These are commonly referred to as VOA vials and are used for many water samples using EPA methods.

6.1.1 The use of 30 mL or smaller VOA vials may allow shipment of multiple sample vials as “excepted quantities” under IATA (International Air Transport Association) regulations. Determine specific shipping requirements with the appropriate knowledgeable personnel.

6.2 *Alternate Containers*—Quartz. Epoxy-lined, tin-lined, or steel cans for direct or sub-sample may not be acceptable because, in some cases, these types of containers show a significant depletion of mercury (see [9.1](#) and [9.2](#)).

6.2.1 Tin-lined steel cans, direct or sub-sample, are not acceptable.

6.3 *Chain of Custody Forms*.

6.4 *Permanent Marking Pens*.

6.5 *Resealable Bags*—Clear, plastic, 1 L capacity.

7. Sampling Procedure

7.1 Employ the normal hydrocarbon sampling procedures necessary to obtain discrete and homogeneous samples. Either grab samples or composites from auto-samplers are allowed. Grab samples are preferred. When expecting particulates with adsorbed mercury or mercury droplets, iso-kinetic sampling is greatly preferred.

7.2 Wash the VOA vials with nitric acid, rinse with water, and dry.

7.3 A sample “set” is defined as three VOA glass vials. Each vial is individually wrapped with a plastic bag, and then the set of three vials are overpacked in an appropriate container for transport or shipping. A set of three individually bagged sample vials may be bundled together and placed in a larger bag to separate them from other sample sets included in the same shipment. Adsorbant material may be packed around the bagged vials to further protect against damage during shipping and release of one or more of the sample vials if it ruptures.

7.4 One sample set is required for each sampling event. Fill three sample vials for each oil sampled as close to the same point in time as possible.

7.5 Sampling shall be done directly into the VOA vials if possible. If it is necessary to sample into one container and then transfer into the VOA vial, record the details of the original container and sampling method, as well as the details of the transfer. Auto-samplers are acceptable, but the container and plumbing materials and transfer details shall be documented in the notebook or Chain of Custody (COC) form.

7.6 Purge sample taps sufficiently immediately prior to sampling to remove any elemental mercury droplets that have accumulated in the piping, valve, or crevices. In some cases, significant amounts of elemental mercury have been found to accumulate in sample taps. Proper collection or recycling of the purge is important to prevent release of mercury and worker exposure.

7.7 It is imperative that persons conducting or supervising the sampling procedure understand the conditions that cause evaporative or other loss of mercury. While bulk mercury droplets are not highly volatile (vapor pressure <1 mmHg at 20 °C) in many hydrocarbons, the dissolved mercury readily evaporates with an apparent vapor pressure similar to butane or pentane. Also, mercury can readily adsorb on many metal surfaces. Sample taps shall not contain process-contact materials composed of copper, zinc, tin, aluminum, brass, bronze, Monel or other alloys containing these metals.

7.8 To avoid loss of mercury vapor from the samples, proceed as follows:

7.8.1 Fill the vial as quickly as possible, filling the vial with, at most, 1 mL remaining.

7.8.2 Cap the vials immediately to minimize time of exposure to the open atmosphere.

7.8.3 In some cases, recapping the vial under a slow stream of nitrogen back in a laboratory hood has been valuable in preventing oxidation of elemental mercury during shipping.

7.9 *COC Form*—The COC form will accompany samples delivered to the laboratory. Record sample containers and plumbing materials information (especially for auto-samplers) in the permanent record or on the COC form. Note sampling details in the permanent record (notebook) and on the COC form, or both. At a minimum, record the following sample data on a permanent record and on the COC form, or both:

7.9.1 Description of the sample point (sample point number, process stream name, physical location, stream temperature and pressure, and the like).

7.9.2 Names and roles of persons in drawing the samples.

7.9.3 Description of the sampling procedure, including:

7.9.3.1 Exact start and end times.

7.9.3.2 Approximate time to fill individual vials.

7.9.3.3 Any subsampling or auto-sampling procedure notes.

7.9.3.4 Ambient conditions (like temperature and precipitation).

7.9.3.5 Physical appearance of the sample when taken and after cooling (for example, clear and bright, or cloudy, or presence of solids or visible mercury droplets).

7.9.3.6 Any problems encountered.

7.10 Allow samples to cool to ambient conditions prior to packing and shipping. Hydrocarbon samples for mercury analysis need not be cooled below ambient temperature. After the samples are at ambient temperature, examine the cap and septum. If cooling has produced a major distortion of the septum, loosen the cap to allow the head-space vacuum (or pressure) to equilibrate. Allow a minimum amount of air (or a slow sweep of nitrogen) ingress to eliminate the vacuum, then tighten the cap thoroughly.

7.11 Affix labels to each sample vial either before or after sampling each set. Clean the vial exterior to remove any oil. Labels shall include sample identification details and date of sampling, as well as the identity of the person responsible for collecting the sample.

7.12 Place each of the three vials in a separate plastic bag. The set of vials can also be overpacked into a larger resealable plastic bag.

8. Sample Storage and Stability

8.1 The best container for “total mercury analysis in crude oil” sample storage and stability is glass with PTFE-lined cap (see 6.1).

8.2 The following conditions should be observed for maintaining quality control of samples:

8.2.1 Use appropriate sampling containers as specified in this practice.

8.2.2 Avoid intermediate transfers of the samples from one container to another.

8.2.3 Do not allow excessive air contact during sampling. Mercury, particularly elemental mercury, can volatilize rapidly

and be lost if the sampling flow is highly turbulent or has a long contact with the atmosphere.

8.2.4 Minimize or eliminate the sample container head space. Opinions vary on the best procedure. The most conservative approach is to leave a small head space bubble to allow for expansion, even though the septum capped vials specified in the practice generally have enough flexibility to handle thermal expansion during shipment.

8.2.5 Since stable storage time will vary depending on the mercury species present and storage conditions, the samples should be analyzed immediately after collection or as soon as possible to avoid loss of elemental mercury.

8.2.6 Maintain a proper chain of custody.

8.2.7 Note the sample conditions on arrival at the lab and prior to analysis so as to document the excessive loss of hydrocarbons from previously full containers.

9. Contamination and Interference

9.1 Contamination is a significant issue whenever samples contain the target analytes at the parts-per-billion or low parts-per-million range. For mercury in hydrocarbon samples, a few simple steps should eliminate contamination and interference issues.

9.1.1 The primary source of contamination during this sampling procedure is usually the presence of accumulated mercury droplets that have come out of solution and accumulated in low-lying piping and sample taps. A single droplet can skew a mercury measurement by several orders of magnitude.

9.1.2 To avoid accumulation of mercury or mercury compounds (for example, mercury sulfide precipitates), sample taps shall not be located at the bottom of piping, but rather the taps shall angle upwards from the top or upper half of the piping. They shall be oriented to be self-draining back into the process.

9.1.3 To further reduce the potential for contamination, sample lines, whether draining from the bottom or top of the piping, shall be thoroughly purged prior to use. Exact purge volumes are difficult to specify but, at a minimum, shall be done with the valve wide open, and flushing at least ten times the volume of the sample piping and valve volume beyond the process line.

9.1.4 If possible, visually examine samples or flush liquid to ensure that the flush liquid is running clean prior to sample collection.

9.2 Additional contamination issues arise from the use of improper sample containers. Improper containers can bias the sample results either high (for example, if a container has been previously used and the adsorbed mercury on the container walls not removed), or low (for example, use of uncoated steel or tin-lined steel which adsorb mercury from the sample).

9.3 In general, sample containers for mercury analysis shall not be reused unless specially cleaned and tested as a blank prior to sampling.

9.4 Uncoated metal container shall not be used for any sampling step, even for a short-term holding before transfer to the VOA vials. Stainless steel containers may be used, but they shall be cleaned and rinsed with a mild acid rinse and

thoroughly dried before use. Epoxy-lined steel containers may also be used, and are preferred for larger volume (>1 L).

10. Analysis of Crude Oil

10.1 Two methods for determination of mercury in crude oil are described in Test Methods **D7622** and **D7623**, both based on electrothermal volatilization of mercury species and subsequent atomic spectroscopic determination.

10.2 Repeatability of analysis of these analyses in the 5 ng Hg/mL to 400 ng Hg/mL given in these standards is as follows:

D7622	$0.7147 X^{0.60}$
D7623	$0.4396 X^{0.5864}$

Where X is the average mercury concentration in ng/mL.

10.3 Reproducibility of the analyses has not been determined. Volatility of mercury compounds and elemental mercury present in crude oil has been documented elsewhere.⁴ Further, replicate laboratory analyses on the same sample have found decreases in mercury concentration over time.⁵ Also, see the discussion about mercury occurrence in crude oils above in **1.2** and **1.3**. Because of this, it is not practical to distribute the crude oil samples to laboratories and get reproducible results.

⁴ Giles, H. N. and Mills, C. O., “*Crude Oils: Their Sampling, Analysis, and Evaluation*,” ASTM International Press, West Conshohocken, PA, Manual 68, 2010.

⁵ Wilhelm, S. M., Kirchgessner, D. A., Liang, L., and Kariher, P. H., “Sampling and Analysis of Mercury in Crude Oil,” STP 1468, *Elemental Analysis of Fuels and Lubricants: Recent Advances and Future Prospects*, Nadkarni, R. A., Ed., ASTM International Press, West Conshohocken, PA, 2005.

Hence, the reproducibility of these test methods is not expected to be determined in the near future.

11. Pollution Prevention and Waste Management

11.1 Draw samples in accordance with both the facility requirements and applicable laws and regulations. Appropriate personal protective equipment shall be worn at all times. Return purge streams directly to the process, or collect for disposal or recycling.

11.2 Free elemental mercury, collected as a separate material or contained with the hydrocarbon sample, shall be treated with extreme caution. Personal exposure to vapors from free mercury droplets or puddles can exceed exposure limits. Appropriate personal protective equipment shall be worn by the sampling team whenever exposure is possible.

11.3 Elemental mercury can be collected (for example, using a mercury vacuum) for disposal, or rendered less hazardous by treating with various sulfur compounds or finely dispersed metal powders (for example, zinc, when activated by mild acid wash) to convert it to less-volatile and less toxic compounds. Facility procedures for responding to releases of elemental mercury shall be applied.

11.4 Disposal of mercury-contaminated materials, elemental mercury, or mercury compounds shall be referred to the facility hazardous waste coordinator.

12. Keywords

12.1 handling; mercury; mercury analysis; sampling; storage

BIBLIOGRAPHY

- (1) Bloom, N. S., *Fresenius Journal of Analytical Chemistry*, Vol 366, 2000, pp. 438–443.

SUMMARY OF CHANGES

Subcommittee D02.03 has identified the location of selected changes to this standard since the last issue (D7482 – 15) that may impact the use of this standard. (Approved July 1, 2017.)

(1) Information on the precision of two standard test methods for mercury determination has been added in a new Section **10**.

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