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# Standard Practice for Sampling and Handling Liquid Cyclic Products<sup>1</sup>

This standard is issued under the fixed designation D 3437; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

# 1. Scope

- 1.1 This practice covers procedures for sampling and handling several liquid cyclic products. These specifically cover liquids at ambient temperature and include benzene, toluene, xylenes, cyclohexane, styrene, pyridine, ethylbenzene, isopropylbenzene, and alpha-methylstyrene.
- 1.2 Any person sampling and handling these products should have specific first aid instructions and equipment available for use in the event of personal contact or exposure.
- 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. For specific hazard statements, see Sections 5, 6 and 7.

#### 2. Referenced Documents

- 2.1 ASTM Standards:
- D 56 Test Method for Flash Point by Tag Closed Tester<sup>2</sup>
- D 850 Test Method for Distillation of Industrial Aromatic Hydrocarbons and Related Materials<sup>3</sup>
- D 3505 Test Method for Density or Relative Density of Pure Liquid Chemicals<sup>3</sup>
- E 300 Practice for Sampling Industrial Chemicals<sup>4</sup>
- 2.2 American National Standards Institute Standard:
- Z 288.1 Flammable and Combustible Liquids Code<sup>5</sup>
- 2.3 API Document:6
- RP-500A Classification of Locations for Electrical Installations in Petroleum Refineries<sup>6</sup>
- 2.4 Other Documents:

OSHA Regulations, 29 CFR paragraphs 1910.1000 and 1910.2000<sup>7</sup>

OSHA Benzene Standard, 29 CFR 1910.1028<sup>7</sup>

U.S. DOT Regulations, 49 CFR Transportation, Subchapter
 C, Parts 171-180<sup>7</sup>

DOT/USCG 46 CFR Subchapter O, Part 1717

## 3. Significance and Use

3.1 This practice is issued to provide information useful in establishing sampling and handling procedures. It is expected that this information will only be utilized in conjunction with an existing health and safety program. The information provided herein cannot be used as a substitute for expert safety and medical advice, but rather as a supplement to such advice.

## 4. Description of Products (See Table 1)

- 4.1 These liquids are marketed in different grades of purity so the physical properties may vary slightly.
- 4.2 The products listed in Table 1 are classified by the Department of Transportation as flammable liquids, and containers must bear flammable liquid labels. Trucks and tank cars must have flammable liquid placards.
- 4.2.1 These products are ordinarily transported in steel drums, tank cars, tank trucks, barges and ships.
- 4.2.2 While these products are dangerous when handled improperly, their unloading need not be hazardous providing the hazards are recognized and handling instructions are rigidly observed.
- 4.3 Products shipped by air must be packaged to meet IATA and ICAO requirements.

## 5. Hazards

- 5.1 *Health*—Consult current OSHA regulations, supplier's Material Safety Data Sheets, and local regulations for all materials used in this practice.
  - 5.2 *Fire*:
- 5.2.1 All of these liquids introduce a potential fire hazard where they are stored, handled, or used.
- 5.2.2 Vapors of all of these materials can form explosive mixtures with air.

<sup>&</sup>lt;sup>1</sup> This practice is under the jurisdiction of ASTM Committee D16 on Aromatic Hydrocarbons and Related Chemicals and is the direct responsibility of Subcommittee D16.08 on Handling and Sampling Aromatic and Cyclic Hydrocarbons.

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<sup>&</sup>lt;sup>2</sup> Annual Book of ASTM Standards, Vol 05.01.

<sup>&</sup>lt;sup>3</sup> Annual Book of ASTM Standards, Vol 06.04.

<sup>&</sup>lt;sup>4</sup> Annual Book of ASTM Standards, Vol 15.05.

<sup>&</sup>lt;sup>5</sup> Available from American National Standards Institute, 11 W. 42nd St., 13th Floor, New York, NY 10036.

 $<sup>^6</sup>$  Available from American Petroleum Institute, 1220 L St. NW, Washington, DC 20005.

 $<sup>^7\,\</sup>mathrm{Available}$  from Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

#### **TABLE 1 Physical Properties**

Product	Boiling Point, <sup>A</sup> °C	Solidification Point, <sup>B</sup> °C	Flash Point <sup>C</sup> Closed Cup, °C	Reid Vapor Pressure Characteristics, <sup>B</sup> psia	Relative Density, <sup>D</sup> 15.56/15.56°C	Odor Threshold, <sup>B</sup> ppm	Explosion Limit <sup>B</sup> Lower	Explosion Limit <sup>B</sup> Higher	Ignition Temperature <sup>B</sup> ° F
Benzene	80	5.5	-11	3.22	0.88	4.7	1.3	7.9	1097
Cyclohexane	80	6.6	-17	3.3	0.78	2.5	1.3	8.4	518
Ethylbenzene	136	-95	15	0.4	0.87	140	1.0	6.7	860
Isopropylbenzene	152	-96	46	0.5	0.87	1.2	0.9	6.5	797
Pyridine	115	-42	20	0.77	0.99	0.02	1.8	12.4	900
Styrene	145	-30	31	0.27	0.91	0.15	1.1	6.1	914
Toluene	110	-95	4	1.1	0.87	0.17	1.3	7.0	997
Xylene (mixed)	137 to 144	-65	27	0.4	0.87	0.05	1.0	7.0	977
o-Xylene	144	-25	17	0.28	0.88	0.05	1.1	7.0	869
<i>p</i> –Xylene	138	13	27	0.34	0.87	0.05	1.1	6.6	870
alpha-Methyl Styrene	165	-23	45	0.23	0.91	<10	1.9	6.1	1066

<sup>&</sup>lt;sup>A</sup>See Test Method D 850.

- 5.2.3 Foam, carbon dioxide, dry chemical, or water fog can be used in fighting fires of these products. Special alcohol-type foam is required to extinguish effectively a fire involving pyridine.
- 5.3 For chemical emergency (spill, leak, fire, exposure, accident), call CHEMTREC day or night at 1-800-424-9300. For emergency calls outside the United States, call 703-527-3887. (Collect calls are accepted and all calls are recorded.)

## 6. Protection Equipment

- 6.1 Employees who work with the chemicals listed in Table 1 should be trained and should maintain safe working conditions. Persons working with these chemicals require eye, face, body protection, and, for benzene, various types of respiratory protection that is dictated by the amount of exposure. Consult MSDS for more specific recommendations.
- 6.2 Personal protective equipment is not an adequate substitute for good safe working conditions, proper ventilation, and intelligent conduct. Correct usage of protection equipment requires education in proper use.

#### 7. Safety Precautions

- 7.1 Unloading, loading and sampling operations must be conducted by carefully instructed employees and only when adequate lighting is provided.
- 7.2 Be sure that the storage tank is safely vented before connecting the unloading line.
- 7.3 Take extreme care to prevent spills and leaks. In case material is spilled, wash contaminated areas thoroughly with large quantities of water and collect the liquid in the plant chemical waste system. All spill-related activities should comply with applicable EPA, OSHA and local regulations and laws.
- 7.4 Because of the flammability of vapors, do not permit sparks or open flames in the vicinity of barges, ships, tank cars, tank trucks, drums, or storage tanks. All electrical equipment and wiring shall be of a type specified by and shall be installed in accordance with the National Electrical Code after determining whether or not the operation is carried out in a classified or unclassified area for electrical installations. Elec-

trically bond tank cars, tank trucks, and drums by an approved method. Smoking is absolutely prohibited.

Note 1—See API-RP500A and ANSI Z 288.1, Chapters VI and VIII, on electric installations.

- 7.5 Do not permit workmen to enter an empty storage vessel, barge, ship, tank car, or tank truck until it has been thoroughly washed out with warm water, followed by a thorough steaming, and the tank atmosphere analyzed for oxygen as well as flammables. Entry should not be made without respiratory protection if the vapor space is not in compliance with OSHA TWA values. SUPERVISOR'S APPROVAL FOR ENTRY IS REQUIRED IN EVERY CASE.
- 7.6 Employees handling benzene must be trained annually to meet the requirements of OSHA Benzene Standard (29 CFR 1910.1028) and wear the respiratory protection listed.
  - 7.7 Employees shall:
- 7.7.1 Know the hazards connected with the handling of specific products;
- 7.7.2 Be completely acquainted with the purpose, use, and maintenance of personal protective equipment;
- 7.7.3 Be trained to report promptly to supervision all suspected leaks or equipment failures;
- 7.7.4 Be trained to recognize and report any symptoms of systemic poisoning or skin contact; be thoroughly trained in the proper procedures for administering first aid and for obtaining professional medical help;
- 7.7.5 Know and routinely practice the accepted methods of sampling and handling these materials in order to avoid spilling or splashing, leaks, skin contact, vapor or mist inhalation, or ingestion;
- 7.7.6 Be completely familiar with the location and operation of safety showers, eye baths, hose lines, and all other first aid equipment; and
- 7.7.7 Know the importance of personal cleanliness and the necessity for immediate removal of clothing contaminated with these products.

## 8. Unloading and Sampling of Tank Cars

8.1 Unloading:

<sup>&</sup>lt;sup>B</sup>Weiss, G., Hazardous Chemicals Data Book, Second Edition.

<sup>&</sup>lt;sup>C</sup>See Test Method D 56.

<sup>&</sup>lt;sup>D</sup>See Test Method D 3505.

- 8.1.1 Because of the flammable properties of these materials, the unloading of tank cars containing chemicals is a hazardous operation. Carefully read and follow all shipper's instructions and all caution markings on both sides of the tank and dome.
- 8.1.2 Before removing the manhole cover or outlet valve cap, relieve the tank car of all internal pressure by venting the tank. This can be accomplished by raising the safety valve, or opening the vent on the dome at short intervals. If venting to relieve pressure will cause a dangerous amount of vapor to escape, defer venting and unloading until the pressure is reduced by allowing the car to stand overnight or otherwise cooling the contents.
- 8.1.3 Use bonding facilities for protection against static sparks during the unloading of tank cars through open domes. This shall consist of a bond wire permanently electrically connected to the unloading pipe or some part of the structure in electrical contact with the unloading pipe. Provide the free end of such wire with a clamp or equivalent device for convenient attachment to some metallic part of the tank car. Such bonding connection shall be made fast to the tank car before dome covers are raised and shall remain in place until unloading is complete and all dome covers closed and secure. This bond wire is not required when the unloading pipe is all metal and the unloading pipe is electrically bonded to the rail tracks.

Note 2-See ANSI Z 288.1, Chapter VI.

8.1.4 Tank cars can be unloaded through the dome connection or through the bottom outlet. Never use air pressure for this purpose. Use of a pump or nitrogen pressure are the recommended methods. If the car does not have an eduction pipe, insert one and remove the contents by pumping. If it is necessary to leave the car unattended after unloading has been started, disconnect all unloading connections. First close all valves tightly and apply the closures to all other openings securely.

8.2 Sampling:

8.2.1 Samples may be taken through the manway opening by means of a clean, dry, 1-qt (1-L) bottle held in a clean, dry sheath of nickel or stainless steel attached to a long rod or lightweight chain of the same material. Fit the bottle with a glass stopper to which is attached a light metal chain. Lower the bottle to near the bottom of the tank and pull out the stopper

with a sharp jerk of the chain. Raise it at such a rate that it is about three fourths full when it emerges from the liquid. Stopper the bottle before attempting to rinse the material from the outside. Label the sample bottle according to OSHA Regulations.

- 8.2.2 Label the sample container to indicate, as a minimum, the date and time, source of the sample, type of material, quantity, hazards, purpose of the sample and the name of the samples.
- 8.2.3 Emphasis should be placed on cleanliness and dryness. Both the sample bottle and its holder must be CLEAN AND DRY. Transfer the sample to another bottle for storage. A suitable bottle for storing the sample is one known as a "Boston Round." The closure should be a screw cap with poly-seal or an aluminum foil liner.
- 8.2.4 If new bottles are used, first rinse them thoroughly with acetone or methanol and then dry in an explosive-proof hot-air oven. Hold in a desiccator while cooling to ambient temperature. Protect them from dirt or moisture by enclosure in a polyethylene bag. Rinse used bottles very thoroughly with water, detergents, and solvents and then treat as new bottles.

Note 3—Brown bottles are recommended for sampling and storing photo-sensitive products.

#### 8.3 Return Precautions:

8.3.1 As soon as the tank car is completely unloaded, close all valves tightly, remove the unloading connections, and make all other closures tight, except the heater coil and steam connections. Observe DOT regulations concerning return placarding. Table 2 is information for loading and unloading vessels.

## 9. Unloading and Sampling of Tank Trucks

- 9.1 Unloading:
- 9.1.1 Because of the flammable properties of these materials, the unloading of tank trucks containing them is a hazardous operation. Follow the DOT regulations, shipper's instructions and all caution markings.
- 9.1.2 Stop the engine before unloading a truck, and do not start it again during the entire unloading operation unless it is necessary to operate the pump by power take-off. Set truck brakes and block the wheels.

#### **TABLE 2 Bulk Packaging Information**

Note 1—Single packagings not permitted on passenger aircraft per the International Civil Aviation Organization Technical Instructions for the Safe Transport of Dangerous Goods By Air and the International Air Transport Association Dangerous Goods Regulations.

Note 2—RQ=100 lb for mixed- and p-xylene and 1000 lb for o- and m-xylene.

DOT basic	RQ lb	Listed Marine Pollutant?	Packaging Authorization 40 CFR 173*			Label(s)	Placards	Remarks
description			Exception	Non-bulk	Bulk	Label(s)	riacaius	Remarks
Benzene, 3, UN1114, II	10	No	150	202	242	flammable liquid	flammable	see Note 1
Toulene, 3, UN1294, II	1000	No	150	202	242	flammable liquid	flammable	see Note 1
Xylene, 3, UN1307, II	100	No	150	202	242	flammable liquid	flammable	see Notes 1 and 2
Xylene, 3, UN1307, III	100	No	150	203	242	flammable liquid	flammable	see Note 2
Cyclohexane, 3, UN1145, II	1000	No	150	202	242	flammable liquid	flammable	see Note 1
Styrene monomer, inhibited, 3, UN2055, III	1000	Yes	150	203	242	flammable liquid	flammable	
Pyridine, 3, UN1228, II	1000	No	None	202	242	flammable liquid	flammable	see Note 1
Ethylbenzene, 3, UN1175, II	1000	No	150	202	242	flammable liquid	flammable	see Note 1
Isopropylbenzene, 3, UN1918, II	5000	Yes	150	203	241*	flammable liquid	flammable	*flash point >38°C
Isopropenylbenzene, 3, UN2303, II	N/A	Yes	150	203	241*	flammable liquid	flammable	*flash point >38°C

- 9.1.3 Before making any connection or contact between the tank truck and the unloading line or other unloading equipment, electrically bond the tank truck in a manner similar to that for tank cars as described in 8.1.3.
- 9.1.4 Tank trucks can be either top or bottom unloaded in the same manner as for tank cars as described in 8.1.4.
- 9.1.5 Air pressure is not permissible for unloading tank trucks of these materials. Nitrogen pressure is permissible for this purpose.
  - 9.2 Sampling:
- 9.2.1 Sample a tank truck in the same way as tank cars, with the same rigid adherence to the precautions against moisture and color degradation.
  - 9.2.2 Label sample containers as described in 8.2.2.

## 10. Unloading and Sampling of Drums

- 10.1 Unloading:
- 10.1.1 When a carload or truckload of drums is received, open the truck doors or the doors on both sides of the car, as the case may be, to allow thorough ventilation of the vehicle before entering it. Examine each shipment for leaking drums. Remove all potential sources of ignition from the area.
- 10.1.2 Before drums are opened, they should be properly supported. Products should not be dispensed from drums into metal containers unless the nozzle or fill pipe is in electrical contact with the container. This can be accomplished by maintaining metallic contact during filling, by a bond wire between them, or by other conductive paths having an electrical resistance not greater than  $10^6\ \Omega$ . Bonding is not required where a container is filled through a closed system, or is made of glass or other nonconducting material.
- 10.1.3 It is necessary that the operator wear goggles and use a bung or plug wrench when removing the body plug from a drum of one of these materials. Place the drum upright, stand to one side, and turn the face away during the operation. After the plug starts to loosen, give it not more than one full turn. If internal pressure exists, allow it to escape to the atmosphere. Then loosen the plug further and remove it.
- 10.1.4 The preferable safe method for emptying drums is by hand pump. If an electrical pump is used, it shall be installed in accordance with the National Electrical Code and shall be suitable for the electrical classification of the area in which it is located. If these drums are emptied by gravity, the faucets must be self-closing. The use of pressure for emptying drums is not recommended.
  - 10.2 Sampling:
- 10.2.1 The use of a stainless steel sampling tube is recommended for drum sampling. The tube should be designed so that it will be within about 1 in. (25 mm) of the bottom and have a suitable capacity. (A detailed description of drum sampling tube is given in Practice E 300.) Insert the open tube through the top bung of an upright drum and lower it to the bottom. With the thumb over the upper opening, withdraw the tube quickly and transfer the contents into a bottle.
- 10.2.2 Clean and dry the bottles in the same manner as the tank car sampling bottles.

## 11. Unloading and Sampling Barges and Ships

- 11.1 Sample and handle barges and ships in a manner similar to top unloading of tank cars and tank trucks (see 8.1.4).
- 11.2 The shipment of benzene by barge is regulated by the U.S. Coast Guard. Barges used for transporting benzene are regulated by 46 CFR Subchapter O, Part 151 as a dangerous cargo.

# 12. Sampling Process Streams

- 12.1 Laboratory Test Samples:
- 12.1.1 Samples may be taken through process sample valves in clean, dry bottles of appropriate size or in appropriate pressure cylinders if the sample is extracted from a process operating at elevated pressure. Whether or not a sample loop is used, the sample points must be sufficiently purged immediately prior to sample, to ensure a representative sample. Sample systems should meet regulatory requirements.
- 12.1.2 Label sample containers as described in 8.2.2 as soon as possible after being collected and before custody is transferred.
- 12.1.3 Sample containers should be properly designed and sealed to prevent leakage or other forms of sample integrity degradation.
- Note 4—Care should be given to sampling of uninhibited styrene and AMS samples. Amber bottles are recommended for these samples. Uninhibited samples should be quickly inhibited after sampling or analyzed and disposed of promptly.
- 12.1.4 The physical or chemical properties, or both, that are to be measured (for example, physical phase, pH, dispersion of gas or particulates, etc.) should not be changed in the sampling system unless specifically required by the analysis.
- 12.1.5 Particular care should be taken to avoid sampling where there is a possibility of contamination, or where pockets of non-sample materials may accumulate in the plant stream.
- 12.1.6 Typically a sample tap should be in a run of process pipe approximately 10 pipe diameters from an elbow, valve, orifice, or similar flow disturbing device in order to avoid areas of possible cavitation or physical segregation of the process stream. The sample connection should be taken at a location where debris does not accumulate. The sample may be taken with a probe extending into the process pipe approximately one-third to one-half of the diameter so as to extract as representative a sample of the process as possible. Care should be taken such that the probe does not cause a flow disturbance that may lead to segregation of the sample.
  - 12.2 Sampling for On-line Analyzers:
- 12.2.1 A sample circulating system (fast circulating loop) from one point in the process to another point in the process, with sample usually removed via a bypass filter within the loop, is recommended for on-line analysis of process and product streams.
- 12.2.2 The sizing of the sample line to the analyzer should be such that the lag time from the sample tap to the analyzer is consistent with the dynamics of the process being sampled. Facilities should be provided to indicate and regulate adequate flow in the loop.

- 12.2.3 Where possible fast circulating loops should take advantage of pressure differentials in the process, for example, across process pumps (drawing from downstream of the pump discharge and returning upstream of the pump suction). Care should be taken to avoid setting sample collection points across valves that have a critical tight shutoff requirement.
- 12.2.4 The sample stream from the fast loop fed to the analyzer should normally be filtered through a self-cleaning bypass filter.
- 12.2.5 The physical or chemical properties, or both, that are to be measured (for example, physical phase, pH, dispersion of gas or particulates, etc.) should not be changed in the sampling system unless specifically required by the analysis.
- 12.2.6 Particular care should be taken to avoid sampling where there is a possibility of contamination, or where pockets of non-sample materials may accumulate in the plant stream.
- 12.2.7 Typically a sample tap should be in a run of process pipe approximately 10 pipe diameters from an elbow, valve,

orifice, or similar flow disturbing device in order to avoid areas of possible cavitation or physical segregation of the process stream. The sample connection should be taken at a location where debris does not accumulate; low points in pipe runs or in the pipes themselves are therefore not desirable. The sample may be taken with a probe extending into the process pipe approximately one-third to one-half of the diameter so as to extract as representative a sample of the process as possible. Care should be taken such that the probe does not cause a flow disturbance that may lead to segregation of the sample.

12.2.8 The sample line should be designed to be consistent with local environmental conditions and with the requirements of the analyzer it is feeding, for example, heat tracing for freeze protection, cooling for bubble point reduction. The analyzer vender should be consulted for sampling system assistance.

## 13. Keywords

13.1 aromatics; handling; sampling

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