Designation: D7938 – 15

Standard Practice for Sampling of C-14 in Gaseous Effluents[1]

This standard is issued under the fixed designation D7938; 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 The intended use of this practice is for sampling of gasses containing ^{14}C in inorganic, organic or particulate forms. This sampling practice captures the ^{14}C in a media that can be submitted to a laboratory for analysis, typically by liquid scintillation counting (LSC)

1.2 This practice does not include the needed steps for the liberation of ^{14}C from the media on which it was adsorbed or those for the preparation for LSC sample preparation in the laboratory prior to liquid scintillation analysis. This practice does not include the methodology used to analyze the prepared samples by LSC.

1.3 The overall ^{14}C analytical detection capability is impacted by a number of factors including the volume sampled, the method used to desorb the ^{14}C from the media, and the analytical method used the measure ^{14}C from the media. This practice only directly addresses the volume of the gas stream from which any present ^{14}C would be adsorbed.

1.4 The values stated in pCi units are to be regarded as standard given the reporting requirements of the U.S. NRC Regulatory Guide 1.21. The Bq values given in parenthesis are mathematical conversions to SI units that are provided for information only and are not considered standard. Other values stated in SI units are to be regarded as 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 and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D1129 Terminology Relating to Water

D7282 Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements

D7902 Terminology for Radiochemical Analyses

2.2 *U.S. NRC Publications:*[3]

U.S. NRC Regulatory Guide 1.21 "Measuring, Evaluating, and Reporting Radioactive Material in Liquid and Gaseous Effluents and Solid Waste," revision 2, June 2009

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms used in this standard, refer to Terminologies D1129 and D7902.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *organic ^{14}C, n*—any gaseous, chemical ^{14}C form (including CO) that is not particulate and not CO_2.

3.2.1.1 *Discussion*—Although no specific organic form is determined, the major contributors are likely to be CH_4, C_2H_6, C_2H_4, CO, and C_2H_2.

3.2.2 *inorganic ^{14}C, n*—the gaseous, chemical form of ^{14}C as CO_2.

3.2.2.1 *Discussion*—These chemical form categorizations are based on U.S. NRC Regulatory Guide 1.21.

4. Summary of Practice

4.1 A sample of a flowing gaseous stream is extracted at a flow rate of 30 to 3000 mL/min. The sample is filtered, and split into two parallel flow paths. One flow path is passed through a furnace to convert all carbon to CO_2. This will yield a total ^{14}C content of the sample. The other flow path collects only the CO_2 fraction of the gaseous stream. This yields the inorganic ^{14}C content of the gaseous stream. The calculated difference between the measured total and inorganic carbon

---

[1] This practice is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

Current edition approved Dec. 15, 2015. Published February 2016. DOI: 10.1520/D7938-15.

[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 U.S. Nuclear Regulatory Commission, Washington, DC 20555-0001, http://www.nrc.gov.

content is the organic content (U.S. NRC Regulatory Guide 1.21). The concentration of ^{14}C in the particulate matter may also be determined.

5. Significance and Use

5.1 This practice was developed[4] for the purpose of sampling gaseous effluent streams from a facility that releases ^{14}C in either organic or inorganic forms.

5.1.1 For many years ^{14}C was not included in gaseous and liquid effluent measurements used for effluent dose calculations at nuclear power facilities. U.S. NRC Regulatory Guide 1.21 now requires ^{14}C analysis (either estimated by calculation or actual measurement) and its impact on annual dose in the environs of nuclear plants be evaluated. Based on the revisions to the Regulatory Guide and NRC guidance to licensees, ^{14}C activity will need to be reported and evaluated for dose contribution based on the activity concentration and chemical form of the ^{14}C in the release.

5.2 While ^{14}C releases may be estimated, the measurement of actual ^{14}C emissions provides a more reliable and accurate means of reporting emissions. The chemical form of ^{14}C that yields the greatest dose significance due to uptake by living organisms is the inorganic form. Thus the distribution of ^{14}C chemical forms in plant effluents is important in assessing the overall dose impact.

5.3 Use of this sampling practice has identified that for pressurized water reactors (PWRs) >90 % of all ^{14}C released may be in the *organic* form during operation, and for boiling water reactors (BWRs) <30 % of all ^{14}C released may be in the *organic* form during operation.

5.3.1 Some power plants have catalytic hydrogen recombiners in the waste gas processing system. These can also oxidize organic carbon to CO_2, increasing the percentage of $^{14}CO_2$ in the effluent release.

5.3.2 During refueling outages, oxidizing conditions exist in the reactor cavity due to air saturation and radiolytic reactions by the nuclear fuel. The combination of these two effects has been shown to increase the $^{14}CO_2$ content of the sampled atmosphere inside the containment building.

5.4 The sampling methodology described in this practice is not capable of discriminating between *different* organic forms of ^{14}C.

6. Interferences

6.1 Based on the chemical methodology used in this sampling practice, interference from non-volatile radionuclides is eliminated. However, the radon progeny of the uranium (^{222}Rn), thorium (^{220}Rn), and actinium (^{219}Rn) series may be possible interferences. Their contribution to the liquid scintillation activity of the samples should be assessed by an independent radiological method (for example, gamma ray spectrometry, or monitoring the liquid scintillation region above the ^{14}C window).

6.2 Gaseous flow paths with carbon dioxide concentrations greater than those found in routine atmospheric samples may raise the detection limit for ^{14}C. This would require a lower sample volume ensuring that the adsorbent does not become saturated with stable CO_2, allowing bypass of the $^{14}CO_2$.

6.3 Tritium can interfere with the analysis of ^{14}C by LSC. Tritium (when present as part of a water molecule) is effectively removed during the sampling collection process using a desiccant upstream of the carbon dioxide trap.

6.3.1 Tritium removal can also be accomplished during the sample preparation step in the laboratory by using a water trap with HCl prior to the final carbon dioxide trap (see Fig. X1.1).

6.4 High levels of moisture in the gaseous effluent would limit the sample volume raising the detection limit. A method of monitoring the level of depletion of the desiccant material should be employed in this method.

7. Apparatus

7.1 *Combustion Furnace*—Capable of attaining at least 600°C with the air flow at a maximum of 3000 mL/min.

7.1.1 The performance of the converter was determined by independent laboratory tests by measuring the conversion efficiency of methane to CO_2. The conversion efficiency was found to be >95 % over a sample flow rate of 300 to 3000 mL per minute. No reduction in conversion efficiency was observed as a function of methane concentration or flow rate.

7.2 *Air Sampling Pump*—Capacity in the range of 30 to 3,000 mL/min.

7.3 *Two Flow Monitors*—Calibrated for air flow in the desired flow range.

7.4 *Particulate Filter Holder*—Normally sized for a 47–mm diameter filter but may be sized to fit the sample flow.

7.5 *Desiccant Tube*—Sized for the amount of desiccant needed for the volume of air to be sampled.

8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[5] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without increasing the background of the measurement.

8.1.1 Some chemicals, even of high purity, contain naturally occurring radioactive elements, for example, uranium, actinium, thorium, rare earths and potassium compounds. Also, some chemical reagents, including organic compounds, have been found to be contaminated with artificially produced radionuclides. Consequently, when carrier chemicals are used in the analysis of low-radioactivity samples, the radioactivity

---

[4] Holtzclaw, J., "Sample and Analysis Protocol for ^{14}C in Gaseous Effluents," Radioactive Effluent Technical Specifications (RETS) and Radiological Environmental Monitoring Programs (REMP) Workshop, San Jose, CA, June 28–30, 2010.

[5] *Reagent Chemicals, American Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *'AnalaR' Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

of the carriers shall be determined under identical analytical conditions as used for the sample. The radioactivity of the reagents may be considered as background and subtracted from the test sample counting rate. This increased background reduces the sensitivity of the measurement.

8.2 Ascarite II, commercially available[6] solid material for adsorption of CO_2.

8.2.1 The use of another material which will trap carbon dioxide will be acceptable. However validation of the mediums' ability to retain carbon dioxide should be verified.

8.3 Filter medium, 0.45 µm or equivalent, 47–mm diameter (or as needed to fit filter holder). The filter material may be paper, fiberglass, or polymeric.

8.4 Desiccant, commercially available material for water removal.

9. Calibration and Standardization

9.1 Put the flow monitoring instrument into operation according to the manufacturer's instructions.

9.2 Put the combustion furnace into operation following the manufacturer's instructions.

10. Sampling

10.1 In order to differentiate the three different physical plus chemical forms of ^{14}C the sampling apparatus must contain the distinct components shown in Fig. 1.

10.1.1 The system consists of a particulate filter followed by two separate parallel sampling pathways.

10.1.2 The top pathway contains a desiccant for adsorbing water (including tritiated water, ^{3}HOH) prior to the adsorbent for capturing $^{14}CO_2$, a flow meter, and an air sample pump. This pathway will collect $^{14}CO_2$ (inorganic ^{14}C) but not organic ^{14}C.

10.1.3 The bottom pathway is identical to the top pathway except that the first component is a high temperature furnace that converts organic carbon to CO_2. A desiccant is used for adsorbing water (including any tritiated water) prior to the adsorbent. The $^{14}CO_2$ can then be captured by the CO_2 adsorbent. Thus the bottom pathway collects total ^{14}C that has been converted to $^{14}CO_2$. The difference between the amounts of ^{14}C adsorbed in the two pathways is the amount of organic ^{14}C.

10.2 The flow monitoring device should be placed in between the suction of the sample pump and the CO_2 adsorbent material (see Fig. 1). This ensures that any additional flow due to leaks in the pump will not be counted towards the final sample volume.

10.3 Practical sampling times may range from 0.5 hours to more than 10 hours. This depends on the limit of detection desired for the particular flow path and the assumed distribution of ^{14}C between organic and inorganic forms.

10.4 The particulate filter mentioned in 10.1.1 may be used if ^{14}C concentration of the particulate matter is required. Particulate ^{14}C captured on the filtration medium is analyzed separately. If the measurement quality objectives require only total ^{14}C analysis, it is still recommended that the sample be filtered. The particulate filter should be treated separately to ensure the conversion to carbon dioxide will be complete prior to radiochemical analysis.

10.5 The preceding steps in this section of this practice should be used to develop facility specific sampling protocols. Once the samples have been collected they should be submitted for analysis following standardized methods. A description of single operator test data collected using this sampling practice and the selected laboratory analysis method is presented in Appendix X1.

11. Calculation

11.1 A calculation may be required to convert the results of the laboratory analysis to the activity per unit volume sampled.

11.2 The results of the sample analysis will yield both the total ^{14}C and inorganic ^{14}C activity concentration. These values are used for the calculation of organic ^{14}C activity concentration based on Eq 1.

11.3 The lower flow path in Fig. 1 is designated as "Total ^{14}C," while the upper flow path is designated as "Inorganic ^{14}C."

11.4 The organic absolute concentration and fraction of the ^{14}C content of the sample is calculated as:

11.4.1 *Organic Content, pCi/L:*

$$\text{Organic } ^{14}C,\text{pCi/L} = \text{Total } ^{14}\text{C} - \text{Inorganic } ^{14}\text{C} \quad (1)$$

11.4.2 *Organic Percent of Total:*

$$100 \times [\text{Total } ^{14}\text{C } (\text{pCi}/\text{L}) - \text{Inorganic } ^{14}\text{C}(\text{pCi}/\text{L})]/\text{Total } ^{14}\text{C}(\text{pCi}/\text{L}) \quad (2)$$

11.5 The apparatus shown in Fig. X1.1 was used to remove tritium (which would interfere with analysis of ^{14}C) and to sequester the carbon dioxide prior to liquid scintillation analysis for ^{14}C.

12. Quality Control

12.1 *Field Blank:*

12.1.1 Generate a compressed air field blank with each group of no more than 20 field samples. The air should be taken from a compressed air source (preferably a gas cylinder) that has not been part of the ambient environs being sampled.

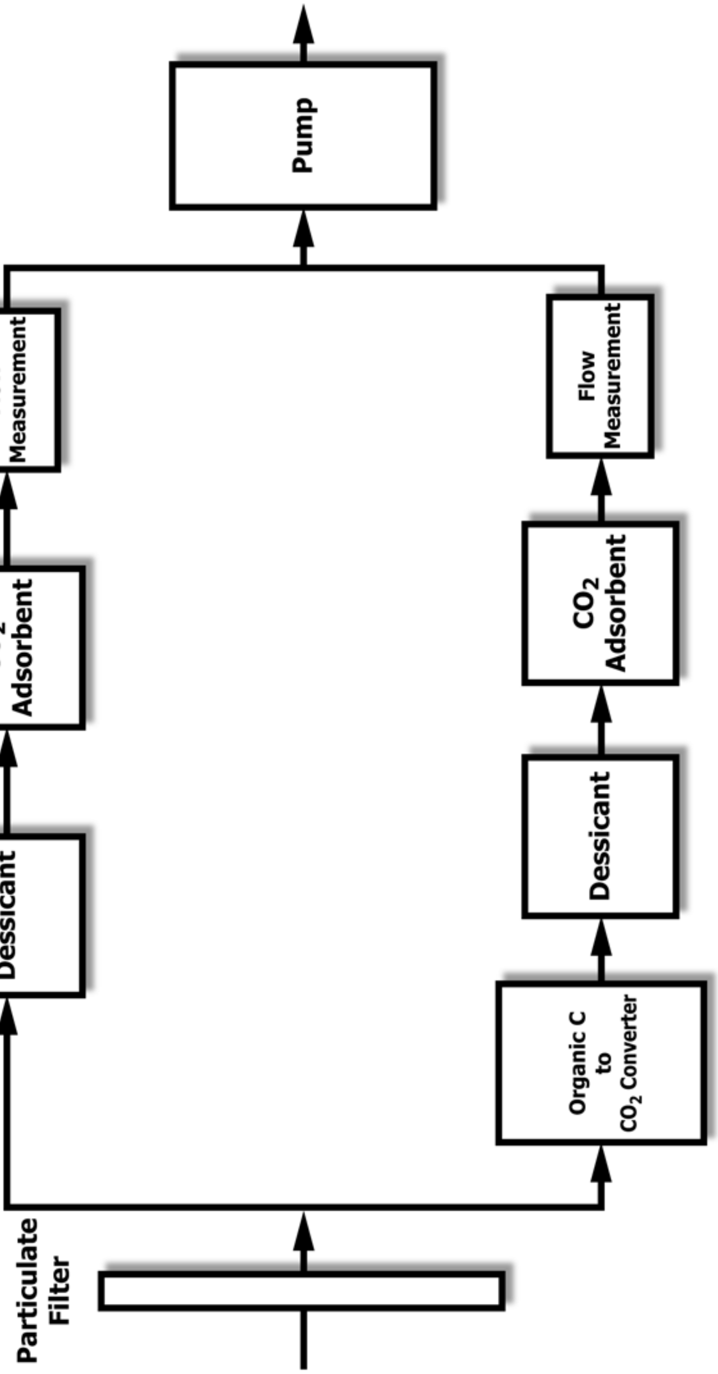
12.1.2 Submit the field blank to the laboratory for analysis with the associated field samples. The concentration of the analyte found in the field blank should be less than one-half of the laboratory reported MDC.

12.2 *Field Duplicate:*

12.2.1 If a field duplicate sample is required, either a second sampling train (as shown in Fig. 1), or a second sampling event taken within a very short time frame (minutes) of the first sample should be employed. Generate a field duplicate with

---

[6] The sole source of supply of the apparatus known to the committee at this time is Arthur H. Thomas Company in Swedesboro, NJ, 08085. If you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee,[1] which you may attend.



NOTE 1—See Holtzclaw, J., "Sample and Analysis Protocol for ^{14}C in Gaseous Effluents," Radioactive Effluent Technical Specifications (RETS) and Radiological Environmental Monitoring Programs (REMP) Workshop, San Jose, CA, June 28–30, 2010.

FIG. 1 Flow of the Gaseous Effluent Sample Through the Sampling Device

each group of not more than 20 samples. These conditions help to ensure representativeness of the duplicate to the original sample.

12.2.2 Calculate the statistical agreement [duplicate error ratio (DER)] between the two results. This calculation is performed using the combined standard uncertainty of each result as shown below:

$$\mathrm{DER} = \frac{\left|\mathrm{AC}_{\mathrm{original}} - \mathrm{AC}_{\mathrm{dup}}\right|}{\sqrt{u_c^2(\mathrm{AC}_{\mathrm{original}}) + u_c^2(\mathrm{AC}_{\mathrm{dup}})}} \quad (3)$$

where:

$\mathrm{AC}_{\mathrm{original}}$ = original sample activity concentration,
$\mathrm{AC}_{\mathrm{dup}}$ = duplicate sample activity concentration,
$u_c{}^2(\mathrm{AC}_{\mathrm{original}})$ = combined standard uncertainty of the original sample, and
$u_c{}^2(\mathrm{AC}_{\mathrm{dup}})$ = combined standard uncertainty of the duplicate sample.

12.2.3 The value of DER should be less than or equal to 3.0.

12.3 *Independent Reference Material (IRM):*

12.3.1 A means of verifying the precision and bias of the laboratory reported sample results can be done by spiking a quantity of carbon dioxide trapping agent packaged in a similar manner as associated field samples with a known quantity of inorganic ^{14}C, and drawing a volume of blank air equivalent to the sample volume, through the trapping agent. Submit the IRM sample to the laboratory for analysis with the associated field samples.

12.3.2 In the absence of other acceptance criteria for the IRM sample, compare the IRM sample result to the IRM known value as follows:

$$Z = \frac{\left|\mathrm{IRM}_{\mathrm{found}} - \mathrm{IRM}_{\mathrm{known}}\right|}{\sqrt{u_c^2(\mathrm{IRM}_{\mathrm{found}}) + u_c^2(\mathrm{IRM}_{\mathrm{known}})}} \tag{4}$$

where:

Z = the z-score for the comparison,
$\mathrm{IRM}_{\mathrm{found}}$ = found concentration of the IRM,
$\mathrm{IRM}_{\mathrm{known}}$ = known concentration of the IRM,
$u_c^2(\mathrm{IRM}_{\mathrm{found}})$ = combined standard uncertainty of the IRM found concentration, and
$u_c^2(\mathrm{IRM}_{\mathrm{known}})$ = combined standard uncertainty of the IRM known.

12.3.3 The value of Z should be less than or equal to 3.0.

13. Keywords

13.1 C-14; gaseous effuents; inorganic ^{14}C; organic ^{14}C

APPENDIX

(Nonmandatory Information)

X1. EXAMPLE DATA

X1.1 Example data generated (with associated uncertainty, k = 2) from samples collected using this practice are shown in Table X1.1. The data are from samples taken at an operating pressurized water reactor (PWR).

X1.2 Steps of the practice were tested using a ^{14}C traceable standard. The analysis of the carbon dioxide absorbent (Fig. 1) for ^{14}C was performed using liquid scintillation counting at one laboratory. The analysis of the carbon dioxide absorbent (Fig. 1) for ^{14}C was performed using liquid scintillation.[7]

X1.3 Direct spikes of Ascarite II[8] were performed with nominal amounts of 71, 717, and 10 500 pCi of ^{14}C. The spikes were added to the process described in the method in various stages:

X1.3.1 *Reagents Only*—^{14}C converted to CO_2 after spiking.

X1.3.2 *Ascarite II*[8]*Plus Reagents*—^{14}C converted to CO_2 after spiking.

TABLE X1.2 Organic and Inorganic ^{14}C Fractions in a PWR Power Plant Effluent

Location	Total, pCi/L	% Organic	% Inorganic
Plant Vent	$(1.39 \pm 0.18) \times 10^0$	99.3	0.7
Waste Gas #1	$(4.50 \pm 0.84) \times 10^6$	91.9	8.1
Waste Gas #2	$(5.56 \pm 0.14) \times 10^6$	96.8	3.2
Waste Gas #3	$(5.26 \pm 0.14) \times 10^6$	93.1	6.9

X1.3.3 $^{14}CO_2$ generated in laboratory and passed through Stage X1.3.2, Ascarite II.[8]

X1.3.4 $^{14}CO_2$ generated in laboratory and passed through furnace then through Stage X1.3.2, Ascarite II.[8]

X1.4 The recovery of ^{14}C in each of these tests was greater than 87 %, with the exception of the 10 500 pCi amounts which had a recovery of greater than 77 %. The standard deviation of the data ranged from 3 to 11 %, the 11 % value again recorded for the highest concentration.

X1.5 The test data for blanks and laboratory control samples were obtained both in the laboratory and at a nuclear plant site. The blanks and QC samples were tested at the plant site to show that contamination of the sampling equipment would not

TABLE X1.1 Analytical Results[A] for QC Samples: In the Laboratory and In the Power Plant

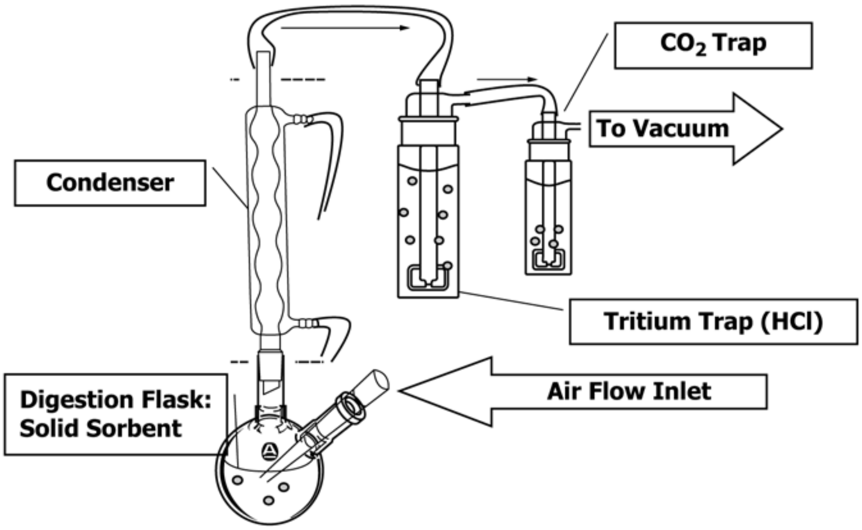
QC	Filter Blank, pCi/L	Ascarite Blank (Total), pCi/L	Ascarite Blank (Inorganic), pCi/L	LCS, pCi/L (Total)[B]	LCS-Dup, pCi/L (Total)[B]
Lab[C]	$-3 \pm 4.1 \times 10^{-2}$ $(-0.11 \pm 0.16 \times 10^{-2})$	$-2.9 \pm 7.8 \times 10^{-2}$ $(-0.11 \pm 0.29 \times 10^{-2})$	$-3 \pm 8.8 \times 10^{-2}$ $(-0.11 \pm 0.33 \times 10^{-2})$	$1.11 \pm 0.08 \times 10^0$ $(4.1 \pm 0.003 \times 10^{-2})$	$1.11 \pm 0.07 \times 10^0$ $(4.1 \pm 0.003 \times 10^{-2})$
Plant[C]	. . .	$1.1 \pm 11 \times 10^{-2}$ $(0.041 \pm 0.41 \times 10^{-2})$	$-7.2 \pm 15 \times 10^{-2}$ $(-0.27 \pm 0.56 \times 10^{-2})$	$1.83 \pm 0.52 \times 10^0$ $(6.77 \pm 0.019 \times 10^{-2})$	$1.87 \pm 0.50 \times 10^0$ $(6.92 \pm 0.018 \times 10^{-2})$

[A] Uncertainties are quoted at a value of k = 2.
[B] Recoveries for these samples was 95 %.
[C] SI Units of Bq/L are in parentheses.

---

[7] General Engineering Laboratories, LLC (GEL), GL-RAD-A-003 Rev 6, "The Determination of Carbon-14 in Water, Soil, Vegetation and Other Solid Matrices."

[8] Ascarite II is a trademark by Arthur H. Thomas Company in Swedesboro, NJ, 08085.



NOTE 1—See Holtzclaw, J., "Sample and Analysis Protocol for ^{14}C in Gaseous Effluents," Radioactive Effluent Technical Specifications (RETS) and Radiological Environmental Monitoring Programs (REMP) Workshop, San Jose, CA, June 28–30, 2010.

FIG. X1.1 Laboratory Distillation Apparatus for Preparation of Sample for ^{14}C Analysis

occur due to the environment. The desiccant tested for these QC samples were spiked using reagent grade water and ^{14}C (for the LCS).

X1.6 The results of blanks and the LCS and their associated uncertainties are shown in Table X1.2.

X1.7 The apparatus used in Fig. X1.1 was used to remove tritium (which would interfere with analysis of ^{14}C) and sequester the carbon dioxide prior to liquid scintillation analysis for ^{14}C.

X1.8 In regard to the ^{14}C analyses performed by the laboratory, reference can be made to Practice D7282 to help assure the proper calibration and quality control of the instrumentation used by the laboratory for that analysis.

ASTM International takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, at the address shown below.

This standard is copyrighted by ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, United States. Individual reprints (single or multiple copies) of this standard may be obtained by contacting ASTM at the above address or at 610-832-9585 (phone), 610-832-9555 (fax), or service@astm.org (e-mail); or through the ASTM website (www.astm.org). Permission rights to photocopy the standard may also be secured from the Copyright Clearance Center, 222 Rosewood Drive, Danvers, MA 01923, Tel: (978) 646-2600; http://www.copyright.com/