Designation: C 1310 – 95 (Reapproved 2001)

Standard Test Method for Determining Radionuclides in Soils by Inductively Coupled Plasma-Mass Spectrometry Using Flow Injection Preconcentration[1]

This standard is issued under the fixed designation C 1310; 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 test method covers a procedure for measuring ^{99}Tc and a procedure for measuring ^{230}Th and ^{234}U in soils. It is applicable to background soils and soils that have been contaminated by nuclear processes. It is intended as an alternative to radiochemical methods because it is faster, requires less labor, and produces less waste than many radiochemical methods.

1.2 Samples are dried, ground, dissolved by fusion, and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). A sequential flow injection (FI) technique is used to provide lower detection limits than those obtained with direct aspiration into an ICP-MS, and, in the case of ^{99}Tc, provides separation from interferences.

1.3 The ^{230}Th and ^{234}U procedure also would work for ^{232}Th, ^{235}U, and ^{238}U, but the FI preconcentration usually is not required to measure these isotopes at the concentrations typically found in soils.

1.4 This test method is guided by quality control procedures derived from U.S. EPA procedures for inorganic analysis reported in SW-846[2] and the Contract Laboratory Program Statement of Work[3]. The required level of quality control may vary between laboratories and projects. Laboratory statistical quality control procedures are required to ensure that this test method is reliable.

1.5 Becquerel (Bq) is the acceptable metric unit for radionuclide activity. However, picocurie (pCi) frequently is the unit used to express regulatory limits for radioactivity. The values stated in either of these units shall be regarded as standard. The values stated in each system may not be exact equivalents; therefore, each system must be used independently of the other, without combining values in any way.

1.6 Refer to Practice C 998 for information on soil sample collection.

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.*

2. Referenced Documents

2.1 *ASTM Standards:*

C 998 Practice for Sampling Surface Soil for Radionuclides[4]

C 1215 Guide for Preparing and Interpreting Precision and Bias Statements in Test Method Standards Used in the Nuclear Industry[4]

D 1193 Specification for Reagent Water[5]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[6]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[7]

2.2 *U.S. EPA Standards:*

SW-846, Test Methods for Evaluating Solid Waste[2]

U.S. EPA Contract Laboratory Program Statement of Work for Inorganic Analysis[3]

3. Terminology

3.1 *Definition:*

3.1.1 *calibration*—refer to Terminology E 135.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *abundance sensitivity*—the characteristic of a mass spectrometer specifying the likelihood of a large peak producing counts at an adjacent mass. It usually is expressed as the number of counts required in the large peak to produce one count at an adjacent mass.

3.2.2 *analyte*—an isotope whose concentration is being determined by the test method.

3.2.3 *calibration blank*—a solution used to establish the zero-concentration calibration point.

3.2.4 *calibration reference solution*—a solution containing known concentrations of the analytes used for instrument calibration.

[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

Current edition approved Nov. 10, 1995. Published March 1996.

[2] Third edition, revision 1, 1992. Available from the U.S. Government Printing Office, Washington, DC 20402.

[3] Document Number ILM01.0. Available from the CLP Sample Management Office, P.O. Box 818, Alexandria, VA 22313.

[4] *Annual Book of ASTM Standards*, Vol 12.01.

[5] *Annual Book of ASTM Standards*, Vol 11.01.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

[7] *Annual Book of ASTM Standards*, Vol 03.05.

3.2.5 *continuing calibration blank check solution (CCB)*—a solution prepared in the same way as the calibration blank that is analyzed at regular intervals to determine if the zero point of the calibration has changed significantly during the analytical run.

3.2.6 *continuing calibration verification check solution (CCV)*—a solution containing the analytes at half the concentrations in the calibration reference solution that is analyzed at regular intervals to verify the accuracy of the calibration throughout the analytical run.

3.2.7 *duplicate specimen analysis*—a second specimen that is treated the same as the original specimen to determine precision of the test method.

3.2.8 *flow injection*—see **sequential flow injection**.

3.2.9 *initial calibration blank check solution (ICB)*—the same as CCB except that it is analyzed immediately after the ICV.

3.2.10 *initial calibration verification check solution (ICV)*—a solution containing known concentrations of the analytes obtained from a source other than that of the calibration reference solution that is analyzed to verify the accuracy of the calibration.

3.2.11 *interference check solution, part A (ICSA)*—a solution containing known concentrations of interfering substances that is analyzed to verify that accurate results can be obtained for a solution that does not contain analyte but contains a relatively high level of interferences.

3.2.12 *interference check solution, part B (ICSAB)*—the same as ICSA, except that it contains known concentrations of the analytes.

3.2.13 *instrument detection limit (IDL)*—the concentration of the analyte equivalent to three times the standard deviation of ten replicate measurements of the calibration blank.

3.2.14 *internal standard*—an element or isotope that is not expected to occur naturally in samples and is added to all sample solutions to serve as a reference to correct for instrument drift and varying chemical recovery through the FI concentration step.

3.2.15 *laboratory control sample (LCS)*—a homogeneous soil sample containing known concentrations of the analytes that is analyzed to verify the accuracy of the test method.

3.2.16 *linear range*—the concentration range over which the analyte signal is linear with respect to its concentration within an established limit.

3.2.17 *linear range check solution (LRS)*—a solution containing known concentrations of the analytes that is used to determine the upper limit of the linear range.

3.2.18 *preparation blank (PB)*—a sample consisting of all the reagents used for sample preparation that is carried through the dissolution and analytical processes to determine if contamination is introduced by the processes.

3.2.19 *relative standard deviation (RSD)*—is expressed in this standard as a percentage, and is calculated by multiplying by 100 the standard deviation of a data set divided by the mean of the data set.

3.2.20 *required detection limit (RDL)*—the instrument detection limit that must be achieved to meet the requirements of the project for which samples are analyzed by this test method.

3.2.21 *RDL check solution*—a solution containing the analytes at a concentration of approximately two times the RDL that is analyzed to assess analytical performance near the RDL.

3.2.22 *specific activity—of a radionuclide*, the numerical value used to convert between units of radioactivity and mass. It is derived from the half-life and the atomic mass of the radionuclide and is expressed as disintegration rate per unit mass.

3.2.23 *sequential flow injection*—an automated non-chromatographic flow analysis technique for concentrating the analytes and separating them from sample components by reproducibly and sequentially manipulating flow of sample and reagents through a column of sorbent material and to the nebulizer of an ICP-MS.

3.2.24 *serial dilution analysis*—a digested specimen that is diluted five-fold with calibration blank solution and analyzed as an indication of the effect of interferences.

3.2.25 *spiked specimen analysis*—a specimen to which a known amount of analyte is added prior to sample dissolution that is analyzed to detect bias of the test method.

4. Summary of Test Method

4.1 The analysis system consists of a computer-controlled FI system attached to the nebulizer of an ICP-MS. The FI system concentrates the analytes by solid-phase extraction and, in the case of ^{99}Tc, provides separation from interferences. The ICP-MS nebulizes the FI eluent into a radio frequency-supported argon plasma that produces, ideally, singly-charged atomic ions that are detected by mass spectrometry. Quadrupole mass spectrometers are most commonly used.

4.2 Soil samples are dried, ground, and blended to achieve homogeneity. For ^{99}Tc analysis, samples are fused with sodium peroxide and dissolved in nitric acid. For ^{230}Th and ^{234}U analysis, samples are fused with lithium metaborate and dissolved in nitric acid.

4.3 Sample solutions are analyzed as follows. Internal standards are added and sample solutions are loaded into the automated sampler of the FI system. Rhenium, ^{229}Th, and ^{233}U are used as internal standards for ^{99}Tc, ^{230}Th, and ^{234}U, respectively. The computer starts the FI program and signals the ICP-MS to read during the elution step. The ion intensity measured at the atomic mass of the analyte, normalized to the intensity of the internal standard, is proportional to the concentration of the analyte in the sample solution. The system is calibrated by analyzing solutions with known analyte concentrations and calculating a calibration equation by regression analysis using the known concentrations and the normalized ion intensities. Sample results are calculated by applying the calibration equation to the normalized ion intensity of the analyte measured in the sample.

4.4 The analysis time for a specimen solution is 3.5 min and a 10-mL portion of specimen solution is consumed in each analysis.

5. Significance and Use

5.1 The test methods in this standard may be used to measure the concentrations of ^{99}Tc, ^{230}Th, and ^{234}U in soil samples. The test methods are applicable to soils that have been contaminated by nuclear-related activities such as uranium ore

processing and uranium enrichment. The FI concentration step reduces detection limits by approximately a factor of ten compared to ICP-MS with conventional sample introduction. Approximate IDLs are listed in Table 1.

6. Interferences

6.1 The test methods contain mechanisms to identify and control all interferences that normally are encountered. The magnitude of the interferences can vary significantly with different instruments. Interferences should be evaluated thoroughly on each ICP-MS system used. A discussion of interference management for each analyte is provided in 6.1.1-6.1.3.6.

6.1.1 *Interference Management for ^{99}Tc Analysis*:

6.1.1.1 The measurement method is subject to interferences from ^{99}Ru because the mass spectrometer cannot distinguish ^{99}Tc from ^{99}Ru. Ruthenium is a very rare element. The average abundance of ruthenium in the earth's crust is on the order of 1 ng/g. The natural abundance of ^{99}Ru is 12.7 %. Naturally occurring ruthenium is not expected to present a serious problem because it is so scarce. Ruthenium-99 is also the stable element to which ^{99}Tc decays by beta-emission. However, ^{99}Ru resulting from ^{99}Tc decay is also expected to be scarce because the half-life of ^{99}Tc is 212,000 years and ^{99}Tc has only been produced from fission for approximately 50 years.

6.1.1.2 High concentrations of molybdenum could cause an interference if the ^{100}Mo peak is large enough to overlap with mass 99 or if formation of $^{98}MoH^+$ is significant. The magnitude of the interference depends on the concentration of molybdenum in the sample, the abundance sensitivity of the ICP-MS in use, and the ratio of MoH^+ to Mo^+.

6.1.1.3 The extraction resin is effective at separating technetium from ruthenium and molybdenum. The separation efficiency varies slightly between extraction columns from approximately 97 % to greater than 99.5 %.

6.1.1.4 The average abundance of molybdenum in the earth's crust is 2 µg/g. The amount of tailing of ^{100}Mo into mass 99 is small when using an ICP-MS with a high abundance sensitivity. The amount of MoH^+ observed relative to Mo^+ is also small, at approximately 0.001 %. Molybdenum is not likely to cause an interference when using an ICP-MS with a high abundance sensitivity.

6.1.1.5 The interference check solutions described in 9.2.4 and 9.2.5 should be analyzed at the beginning and end of each analytical run to verify that separations from molybdenum and ruthenium are effective. Molybdenum-100 and ^{101}Ru should be monitored in each analysis to verify the absence of interferences.

6.1.1.6 Calibration solutions are prepared in a mixture of sodium peroxide and nitric acid in the same amounts used for sample digestion to minimize matrix effects on extraction efficiency of technetium and rhenium.

6.1.2 *Interference Management for ^{230}Th Analysis*:

6.1.2.1 High concentrations of ^{232}Th in samples could interfere with ^{230}Th determinations if the peak at mass 232 is large enough to have a tailing overlap of mass 230. Natural thorium is essentially 100 % ^{232}Th, and any ^{232}Th present in the samples is also concentrated by the flow injection process. The magnitude of the interference depends on the concentration of ^{232}Th in the samples and the abundance sensitivity of the ICP-MS in use.

6.1.2.2 The potential for interference should be determined for each ICP-MS system used by measuring the count rate at mass 230 produced by a series of ^{232}Th standards covering the concentration range of ^{232}Th anticipated in samples.

6.1.2.3 The potential for interference was determined for two different ICP-MS systems. The abundance sensitivity of the ICP-MS having the better rejection of the 232 mass was approximately 30 to 50 times better than the other ICP-MS system. For the ICP-MS having poor rejection for mass 232, ^{232}Th levels equivalent to 20 mg/kg and above produced significant counts at mass 230. The interference scheme described in 6.1.2.4-6.1.2.6 was used. With the second ICP-MS, no interference was observed for ^{232}Th levels equivalent to 500 mg/kg.

6.1.2.4 If ^{232}Th is present at high enough concentration in a sample to tail into mass 230, it will also tail into mass 231. Therefore, the counts observed at mass 231 during an analysis give an indication of the concentration of ^{232}Th in the sample. Monitoring mass 231 to indicate the ^{232}Th concentration is preferable to monitoring mass 232 because the count rate at mass 232 would be several million counts per second if the ^{232}Th concentration is high enough to cause an interference at mass 230.

6.1.2.5 A correction factor can be determined by measuring the ratio of counts at mass 230 to counts at mass 231 for a ^{232}Th standard at a concentration high enough to produce an interference. The factor can be used to correct the counts at mass 230 based on the counts at mass 231. The correction factor should be determined each day at the beginning and end of the analysis run.

6.1.2.6 The interference check solutions described in 9.3.4 and 9.3.5 should be analyzed at the beginning and end of each analytical run to demonstrate that ^{232}Th can be tolerated up to the level present in the check solutions.

6.1.3 *Interference Management for ^{234}U Analysis*:

6.1.3.1 High concentrations of ^{232}Th in samples could also interfere with ^{234}U determinations by producing a peak at mass 233 from ThH^+ that overlaps with ^{233}U which is used as the internal standard. This would result in a negative bias. The amount of ThH^+ observed relative to Th^+ is approximately 0.01 % or less.

6.1.3.2 The potential for interference should be determined for each ICP-MS system used by measuring the count rate at mass 233 produced by a series of ^{232}Th standards covering the concentration range of ^{232}Th anticipated in samples.

6.1.3.3 The potential for interference and correction schemes was evaluated for the two ICP-MS systems described in 6.1.2.3. For both systems, ^{232}Th at levels equivalent to 20 mg/kg and above produced significant counts at mass 233. Slightly different interference correction schemes were developed for the two systems because of the different abundance sensitivities.

6.1.3.4 With the ICP-MS having a lower abundance sensitivity, an interference correction scheme similar to that used for ^{230}Th was found to be adequate. A correction factor can be determined each day by measuring the ratio of counts at mass

233 to counts at mass 231 for a ^{232}Th standard at a concentration high enough to produce an interference. Mass 231 can be monitored in each analysis to indicate the amount of ^{232}Th present in the sample. The correction factor can be used to correct the counts at mass 233 based on the counts at mass 231 if the ^{232}Th concentration is high enough to cause an interference.

6.1.3.5 With the ICP-MS having a higher abundance sensitivity, monitoring mass 231 did not indicate the ^{232}Th concentration because ^{232}Th did not tail into mass 231 unless the concentration was extremely high. Using a correction factor based on the measured ratio of counts at mass 231.5 to counts at mass 233 for a ^{232}Th standard at a high enough concentration to produce an interference was found to be adequate. The selected mass can be monitored in each analysis, and the correction factor can be used as described in 6.1.2.5. The correction factor should be determined each day at the beginning and end of the analysis run.

6.1.3.6 The interference check solutions described in 9.3.4 and 9.3.5 should be analyzed at the beginning and end of each analytical run to demonstrate that ^{232}Th can be tolerated up to the level present in the check solutions.

7. Apparatus

7.1 *Sample Preparation*:

7.1.1 *Pulverizer*—suitable for grinding samples to a particle size that passes through a 45-µm standard test sieve as defined in Specification E 11.

7.1.2 *Blender*—suitable for blending the ground samples to achieve homogeneity.

7.1.3 *Zirconium Crucibles*—with 55-mL capacity used for sodium peroxide fusions for ^{99}Tc analysis.

7.1.4 *Platinum Dishes*—with approximately 5-mL capacity used for lithium metaborate fusions for ^{230}Th and ^{234}U analysis.

7.1.5 *Shaking Hotplate*—with temperature range to at least 150°C that can shake at approximately 100 rpm. This item is used for dissolving lithium metaborate fusions and can be made by mounting a hot plate onto a platform shaker.

7.2 *FI Analysis System Components*:

7.2.1 *FI Analysis System*—equipped with a five-port valve, two multi-channel pumps, autosampler, and having the capability for remote control of a peristaltic pump. The system is interfaced to an ICP-MS for control of valve position and pumps.

7.2.2 *FI Manifold*—Fig. 1 is a schematic of the flow injection manifold showing the tubing arrangement. Construct the manifold with tubing and tubing connectors that are made of polytetrafluoroethylene (PTFE), ethylenetetrafluoroethylene (ETFE), or other material that is inert to nitric acid. Tubing with an outside diameter of approximately 1.6 mm is recommended. Tubing with an interior diameter (ID) of approximately 0.25 mm is recommended from the valve to the nebulizer and approximately 0.76 mm ID is recommended for the remaining tubing.

7.2.3 *Pump Tubing*—with approximately 1.5 mm ID for pumping sample and column rinse solution, approximately 1.1 mm ID for pumping eluent, and approximately 0.76 ID for use with the remote peristaltic pump.

7.2.4 *Extraction Columns*—with a bed volume of approximately 50 µL or larger made from a material that is inert to nitric acid and packed with the extraction resin appropriate for the analysis.

7.2.5 *Peristaltic Pump*—that can be controlled by the FI system to rinse the nebulizer and spray chamber (see Fig. 1).

7.3 *Inductively Coupled Plasma-Mass Spectrometer*—with software and interface to control the FI analysis system. For ^{99}Tc analysis, use a nebulizer and spray chamber that is inert to 50 % (v/v) nitric acid. Ryton is not suitable for long-term use with 50 % (v/v) nitric acid.

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 conform to specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8]

8.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, as defined by Type I, II, or III of Specification D 1193, that is free of detectable concentrations of the analytes.

8.3 *Nitric Acid* (specific gravity 1.42)—Concentrated nitric acid (HNO_3).

8.4 *Additional Reagents and Materials for ^{99}Tc Analysis*:

8.4.1 *Extraction Resin*—Use TEVA·Spec[9] resin.

8.4.2 *High Purity HNO_3* (specific gravity 1.42)—Commercially available concentrated HNO_3 of higher purity than reagent grade, specially prepared by sub-boiling distillation to be low in metallic impurities. High purity HNO_3 is used to prepare the eluent and column rinse solutions because the molybdenum content is usually lower than in reagent grade acid.

8.4.3 *High Purity HNO_3* (50 % v/v)—Add 500 mL of high purity HNO_3 to water, dilute to 1 L, and mix. Use this for the FI eluent.

8.4.4 *High Purity HNO_3* (3 % v/v)—Add 30 mL of high purity HNO_3 to water, dilute to 1 L, and mix. Use this for the FI column rinse solution.

8.4.5 *Sodium Peroxide*(Na_2O_2)—Powder.

8.4.6 *Na_2O_2/HNO_3 Mixture*—Dissolve 22.5 g of Na_2O_2 in approximately 500 to 900 mL of water, add 40 mL of HNO_3, and dilute to 1 L with water. Use for preparing working solutions as indicated in 9.2.

8.5 *Additional Reagents and Materials for ^{230}Th and ^{234}U Analysis*:

8.5.1 *Ammonium Oxalate Solution* (14 g/L)—Dissolve 14 g of ammonium oxalate ($(NH_4)_2C_2O_4·H_2O$) in water, dilute to 1 L with water, and mix. Use this for the FI eluent.

[8] *Reagent Chemicals, American Chemical 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.

[9] TEVA·Spec resin has been found satisfactory for the listed purpose. Available from Eichrom Industries, Inc., P.O. Box 2399, Darien, IL 60559. The procedure for preparing the material has not been published. No other commercial sources of equivalent material are known.

8.5.2 *Extraction Resin*—Either prepare as described by Horwitz et al[10] or use TRU·Spec[11] resin.

8.5.3 *Hydrofluoric Acid* (specific gravity 1.20)—Concentrated hydrofluoric acid (HF).

8.5.4 *Lithium Metaborate* ($LiBO_2$)—Fine powder.

8.5.5 *HNO_3* (25 % v/v)—Add 250 mL of HNO_3 to water, dilute to 1 L, and mix. Use this for the FI column rinse solution.

9. Standards

9.1 *Stock Solutions*—of molybdenum, rhenium, ruthenium, ^{99}Tc, ^{229}Th, ^{230}Th, ^{232}Th, ^{233}U, and ^{234}U may be purchased or prepared from metals, compounds, or other materials of known purity or isotopic composition. The ^{99}Tc, ^{230}Th, and ^{234}U stock solutions for the ICVs should be prepared or obtained from sources other than those of the calibration reference stock solution. The concentration calibrations of the ^{99}Tc, ^{230}Th, and ^{234}U stock solutions should be traceable to a widely recognized standardization organization such as the National Institute of Standards and Technology.

9.2 *Working Solutions for ^{99}Tc Analysis*—The following concentrations are recommended. Prepare all solutions with Na_2O_2/HNO_3 mixture unless indicated otherwise. Prepare the solutions as described in 9.2.1-9.2.6 and 9.2.8 and 9.2.9, and add the internal standard before analysis.

9.2.1 *Calibration Blank, ICB, and CCB*—Na_2O_2/HNO_3 mixture only.

9.2.2 *Calibration Reference and Matrix Spiking Solution*—8 Bq/L (200 pCi/L) ^{99}Tc.

9.2.3 *CCV*—4 Bq/L (100 pCi/L) ^{99}Tc.

9.2.4 *ICSA*—100 µg/L molybdenum and 20 ng/L ruthenium.

9.2.5 *ICSAB*—100 µg/L molybdenum, 20 ng/L ruthenium, and 4 Bq/L (100 pCi/L) ^{99}Tc.

9.2.6 *ICV*—Prepare with ^{99}Tc at a concentration that is within the linear range but different from the calibration reference solution.

9.2.7 *Internal Standard Spiking Solution*—5 µg/L rhenium in 3 % (v/v) HNO_3.

9.2.8 *LRS*—16 Bq/L (400 pCi/L) ^{99}Tc.

9.2.9 *RDL Check Solution*—Prepare at twice the RDL or 0.2 Bq/L (5 pCi/L) ^{99}Tc.

9.3 *Working Solutions for ^{230}Th and ^{234}U Analysis*—The following concentrations are recommended. Prepare all solutions to contain 25 % (v/v) of concentrated HNO_3 in the final solution. Prepare the solutions as described in 9.3.1-9.3.6 and 9.3.8 and 9.3.10, and add the internal standard before analysis.

9.3.1 *Calibration Blank, ICB, and CCB*—25 % (v/v) HNO_3 only.

9.3.2 *Calibration Reference Solution*—30 Bq/L (800 pCi/L) ^{230}Th and 10 Bq/L (300 pCi/L) ^{234}U.

9.3.3 *CCV*—15 Bq/L (400 pCi/L) ^{230}Th and 5 Bq/L (150 pCi/L) ^{234}U.

9.3.4 *ICSA*—1 mg/L ^{232}Th.

9.3.5 *ICSAB*—1 mg/L ^{232}Th, 15 Bq/L (400 pCi/L) ^{230}Th, and 5 Bq/L (150 pCi/L) ^{234}U.

9.3.6 *ICV*—Prepare with ^{230}Th and ^{234}U at concentrations that are within the linear ranges but different from the calibration reference solution.

9.3.7 *Internal Standard Spiking Solution*—20 Bq/mL (500 pCi/mL) ^{229}Th and 15 Bq/mL (400 pCi/mL) ^{233}U.

9.3.8 *LRS*—60 Bq/L (1600 pCi/L) ^{230}Th and 20 Bq/L (600 pCi/L) ^{234}U.

9.3.9 *Matrix Spiking Solution*—3 Bq/mL (80 pCi/mL) ^{230}Th and 1 Bq/mL (30 pCi/mL) ^{234}U.

9.3.10 *RDL Check Solution*—Prepare at twice the RDL or 0.3 Bq/L (8 pCi/L) ^{230}Th and 0.2 Bq/L (6 pCi/L) ^{234}U.

10. Sample Preparation Procedures

10.1 This standard was developed using the sample preparation methods listed in 10.3 and 10.4. These methods are very rigorous and result in essentially complete dissolution of soil samples. Other sample preparation procedures that are suitable for use with the FI-ICP-MS technique including acid digestions with conventional or microwave heating could be developed.

10.2 Dry soil samples in an oven maintained at 103°C to 105°C for 12 to 24 h, grind to a particle size that passes through a 45-µm standard test sieve as defined in Specification E 11, and blend. This results in a homogeneous sample with a particle size that is readily attacked by the fusions.

10.3 *Sodium Peroxide Fusion for ^{99}Tc Analysis*:

10.3.1 Weigh a 0.250 ± 0.002-g specimen into a zirconium crucible.

10.3.2 For the spiked sample, pipet 50 µL of matrix spiking solution onto the sample, dry on a hot plate at 90°C, and break up the sample lump with a small metal spatula.

10.3.3 Add 2.25 g of sodium peroxide to the crucible and mix using the small metal spatula.

10.3.4 Place the crucible on a hearth plate (Note 1), place the hearth plate into an oven that has been preheated to 470°C, and heat for 30 min.

10.3.5 Remove the crucible and hearth plate from the oven, and allow to cool to room temperature.

10.3.6 Place the crucible in a borosilicate glass 250-mL beaker, add approximately 40 mL of water to the crucible, and allow the fusion mixture to dissolve for approximately 1 h until the effervescence stops.

10.3.7 Remove the crucible from the beaker using forceps, and rinse the crucible thoroughly with water into the beaker.

10.3.8 Transfer the sample to a 100-mL graduated cylinder or volumetric flask, rinse the beaker thoroughly into the cylinder or flask with water, and bring the volume to approximately 90 mL with water (Note 2).

10.3.9 Add 4 mL of concentrated HNO_3 to the cylinder or flask, dilute the solution to 100 mL with water, and stir with a glass stirring rod or cap, and shake to mix.

10.3.10 Filter the solution through a 0.45-µm membrane filter to remove turbidity that could plug the extraction column.

10.4 *Lithium Metaborate Fusion for ^{230}Th and ^{234}U Analysis*:

10.4.1 Weigh a 0.500 ± 0.005-g specimen into a platinum dish, and moisten with approximately 1 mL of water. The water

[10] Horwitz, E. P., Chiarizia, R., Dietz, M. L., and Diamond, H.," Separation and Preconcentration of Actinides from Acidic Media by Extraction Chromatography," *Analytica Chimica Acta*, Vol 281, 1993, pp. 361–372.

[11] TRU·Spec resin has been found satisfactory for the listed purpose. Available from Eichrom Industries, Inc., P.O. Box 2399, Darien, IL 60559. No other commercial sources of equivalent material are known.

lessens the severity of the reaction of the specimen with hydrofluoric acid.

10.4.2 For the spiked sample, pipet 0.5 mL of the matrix spiking solution into the dish (Note 3).

10.4.3 Place the dish on a hot plate in a fume hood, add approximately 3 mL of concentrated HF to the dish, and heat at approximately 100°C until dry.

10.4.4 Add a 3-mL portion of HF, and heat again until dry.

10.4.5 Add 1.0 g of $LiBO_2$ to the dish.

10.4.6 Heat the dish over a gas burner in a fume hood to melt the flux. Hold the dish with tongs and rock from side to side to contact the entire specimen with molten flux. Continue heating for approximately 8 min until the specimen is completely attacked.

10.4.7 Carefully drop the hot dish into a borosilicate glass 250-mL beaker containing approximately 30 mL of 25 % (v/v) HNO_3.

10.4.8 Heat the beaker on a shaking hot plate at approximately 100°C and 100 rpm until the fused specimen dissolves (Note 4).

10.4.9 Remove the platinum dish from the beaker with forceps and rinse the dish thoroughly with 25 % (v/v) HNO_3 into the beaker.

10.4.10 Transfer the sample to a 100-mL graduated cylinder or a 50-mL volumetric flask, rinse the beaker thoroughly into the cylinder or flask with 25 % (v/v) HNO_3, dilute to 50 mL with 25 % (v/v) HNO_3, and stir with a glass stirring rod or cap, and shake to mix.

10.4.11 Filter the solution through a 0.45-µm membrane filter to remove the small amount of gelatinous material that forms in some specimen solutions and that could plug the extraction column (Note 5).

NOTE 1—A hearth plate is a plate made of heat-resistant material that can withstand the temperature of the oven. Placing a batch of samples on a hearth plate and loading the plate into the oven is more efficient than loading individual samples. Removing samples from the oven is also more efficient.

NOTE 2—The sample is not completely dissolved at this point, and it will have a slurry-like appearance. Transfer all undissolved material to the graduated cylinder. The sample will dissolve when the nitric acid is added as in 10.3.9.

NOTE 3—The internal standards may be added at this point if monitoring of analyte recovery through the fusion procedure is desired.

NOTE 4—The fused specimen dissolves much faster with a shaking hot plate than with a stationary hot plate.

NOTE 5—The fusion results in essentially complete dissolution of the sample. The small amount of gelatinous material referred to in 10.4.11 is believed to be amorphous silica and has not been known to cause low recovery of the analytes. Removal of the material is necessary because the extraction column frits have small pores that are prone to plugging if any undissolved material is present in the samples.

11. Instrument Set-Up

11.1 Assemble the FI manifold as shown in Fig. 1 and described in 7.2.2. Use a column packed with the appropriate resin for the analysis.

11.2 Fill the reservoirs with the required eluent and column rinse solution. For ^{99}Tc analysis, 50 % v/v high purity HNO_3 is the eluent and 3 % high purity v/v HNO_3 is the column rinse solution. For ^{230}Th and ^{234}U analysis, 14 g/L ammonium oxalate is the eluent and 25 % v/v HNO_3 is the column rinse solution.

11.3 Program the FI system. The FI program performs the following actions: Sample is pumped through the column and to waste to load the analytes onto the resin. The sample residue is rinsed from the column and tubing to waste. The analytes are back-washed from the resin to the nebulizer. The residual eluent is rinsed from the column and tubing to waste and the sample inlet tubing is rinsed to prepare the system for the next sample. An example program and a description of the program steps are given in Table 2. The example program is satisfactory for both test methods.

11.4 Set the ICP-MS instrument operating conditions and data acquisition parameters. Examples are given in Table 3.

12. Instrumental Analysis Procedure

12.1 Specific procedures for operating an FI-ICP-MS are not given in this test method because they vary significantly among the available systems. For vendor-supplied systems, follow the procedures provided by the vendor. Additional information on ICP-MS operation is available in *Applications of Inductively Coupled Plasma Mass Spectrometry*.[12]

12.2 Turn on the ICP-MS system and allow adequate warm-up time.

12.3 Conduct all daily performance checks and optimizations required by laboratory procedures such as tuning, sensitivity, resolution, mass calibration, oxide levels, and doubly charged species levels.

12.4 Attach the FI system to the nebulizer of the ICP-MS and analyze the calibration reference solution in the graphics mode to verify proper system performance. Verify by visual inspection that the peak's appearance time, shape, and size are normal. Verify that the selected integration time is adequate to measure the peak from baseline to baseline. Fig. 2 gives an example of elution profiles for ^{99}Tc and Re reference solutions. Fig. 3 gives an example of elution profiles obtained for ^{229}Th, ^{230}Th, ^{233}U, and ^{234}U reference solutions.

12.5 If ^{230}Th or ^{234}U analyses are being done using correction factors to compensate for ^{232}Th interferences, analyze a 1 mg/L ^{232}Th solution at least in duplicate to determine the correction factors. The correction factor for ^{230}Th is the ratio of blank-subtracted counts at mass 230 to blank-subtracted counts at the mass used to indicate ^{232}Th concentration, such as mass 231 or mass 231.5. The correction factor for ^{233}U is the ratio of blank-subtracted counts at mass 233 to blank-subtracted counts at the mass used to indicate ^{232}Th concentration. Enter the correction factors into the elemental equations for ^{230}Th and ^{233}U.

12.6 Pipet standards and specimen solutions into autosampler tubes, add 0.1 mL of the internal standard spiking solution per 10 mL of standard or specimen solution, mix, and load the tubes into the autosampler.

12.7 Calibrate the instrument with the calibration blank and the calibration reference solution (Note 6).

12.8 Verify the accuracy of the calibration by analyzing the ICV and ICB check solutions, respectively.

[12] *Applications of Inductively Coupled Plasma Mass Spectrometry*, A. R. Date, and A. L. Gray, eds., Blackie and Son Ltd., Glasgow, Scotland, 1989.