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:* [4]
C 998 Practice for Sampling Surface Soil for Radionuclides
D 1193 Specification for Reagent Water
E 11 Specification for Wire Cloth and Sieves for Testing Purposes
E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials

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.

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[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.

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[2] Available from the US EPA at http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm.

[3] Document Number ILM05.0. Available from the US EPA at http://www.epa.gov/superfund/programs/clp/ilm5.htm.

[4] 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.

3.2.5 *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 any 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