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AMERICAN SOCIETY FOR TESTING AND MATERIALS
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Standard Test Method for Analysis of Uranium and Thorium in Soils by Energy Dispersive X-Ray Fluorescence Spectroscopy[1]

This standard is issued under the fixed designation C 1255; 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 the energy dispersive X-ray fluorescence (EDXRF) spectrochemical analysis of trace levels of uranium and thorium in soils. Any sample matrix that differs from the general ground soil composition used for calibration (that is, fertilizer or a sample of mostly rock) would have to be calibrated separately to determine the effect of the different matrix composition.

1.2 The analysis is performed after an initial drying and grinding of the sample, and the results are reported on a dry basis. The sample preparation technique used incorporates into the sample any rocks and organic material present in the soil. This test method of sample preparation differs from other techniques that involve tumbling and sieving the sample.

1.3 Linear calibration is performed over a concentration range from 20 to 1000 µg per gram for uranium and thorium.

1.4 The values stated in SI units are to be regarded as the standard. The inch-pound units in parentheses are for information only.

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:*

C 982 Guide for Selecting Components for Energy Dispersive X-Ray Fluorescence (XRF) Systems[2]

C 998 Practice for Sampling Surface Soil for Radionuclides[2]

D 420 Guide for Investigating and Sampling Soil and Rock[3]

D 1452 Practice for Soil Investigation and Sampling by Auger Borings[3]

D 1586 Test Method for Penetration Test and Split-Barrel Sampling of Soils[3]

D 1587 Practice for Thin-Walled Tube Sampling of Soils[3]

D 2113 Practice for Diamond Core Drilling for Site Investigation[3]

D 3550 Practice for Ring-Lined Barrel Sampling of Soils[3]

D 4697 Guide for Maintaining Test Methods in the User's Laboratory[4]

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials[5]

E 305 Practice for Establishing and Controlling Spectrochemical Analytical Curves[5]

E 456 Terminology Relating to Quality and Statistics[6]

E 876 Practice for Use of Statistics in the Evaluation of Spectrometric Data[7]

E 882 Guide for Accountability and Quality Control in the Chemical Analysis Laboratory[7]

2.2 *Other Document:*

NBS Radiation Safety Handbook Number 111 for X-Ray Diffraction and Fluorescence Analysis Equipment[8]

3. Terminology

3.1 *Definitions:*

3.1.1 For definitions of terms relating to analytical atomic spectroscopy, refer to Terminology E 135.

3.1.2 For definitions of terms relating to statistics refer to Terminology E 456.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *escape peak*—a peak generated by an X-ray having energy greater than 1.84 keV (the energy of the k-alpha absorption edge for silicon) that enters the detector and causes the silicon detector crystal to fluoresce. If the silicon X-ray escapes the detector, carrying with it the energy of the silicon k-alpha X-ray, 2.79 E-16 Joules [J] (1.74 keV), the energy measured for the detected X-ray will be less than the actual X-ray energy by exactly 2.79 E-16 J (1.74 keV). Therefore, as counts accumulate for any major X-ray peak, an escape peak can be expected to appear at an energy of 2.79 E-16 J (1.74 keV) below the major peak. Escape peaks can be calculated and removed from the spectrum by most insrumentation software.

[1] This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Tests.

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

[3] *Annual Book of ASTM Standards*, Vol 04.08.

[4] *Annual Book of ASTM Standards*, Vol 07.02.

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

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

[7] *Annual Book of ASTM Standards*, Vol 03.06.

[8] Available from the U.S. Department of Commerce, National Institute of Standards and Technology, Gaithersburg, MD 20899.

3.2.2 *flux monitor (FM) value*—the detected X-ray intensity within a specified spectral range from a metallic standard giving a high number of counts. The same excitation conditions as the sample analysis are used (except for the change in the current to achieve maximum efficiency of the data acquisition system). With all conditions remaining constant, the FM value is proportional to the X-ray energy flux being emitted from the X-ray tube or radioisotope source.

3.2.3 *flux monitor ratio (FMR)*—the ratio of the initial FM value (FMi) prior to calibration and sample analysis to current FM value (FMc) at the time of sample analysis. This ratio is used to correct the measured element intensity for changes in the X-ray energy flux.

4. Summary of Test Method

4.1 A representative sample of soil is obtained by first taking a sizeable amount (>100 g) and drying it, then running it through a crusher and placing it on a shaker/tumbler to homogenize it. A portion is then ground in a ball mill and pressed into a sample pellet. An energy dispersive X-ray fluorescence spectrometer is used to expose the sample to a monochromatic X-ray source capable of exciting the uranium and thorium L-alpha series lines. The X-rays emitted by the sample are detected via a solid state detector [Si(Li)] and counted in discrete energy channels on a multi-channel analyzer (MCA) to form an energy spectrum. The spectrum is then processed to obtain the peak intensities for uranium and thorium for calibration and quantitation.

5. Significance and Use

5.1 This test method was developed and the instrument calibrated using ground soils from the site of a nuclear materials plant. This test method can be used to measure the extent of contamination from uranium and thorium in ground soils. Since the detection limit of this technique (nominally 20 µg per gram) approaches typical background levels for these contaminants, the method can be used as a quick characterization of an on-site area to indicated points of contamination. Then after cleanup, EDXRF may be used to verify the elimination of contamination or other analysis methods (such as colorimetry, fluoremetry, phosphorescence, etc.) can be used if it is necessary to test for cleanup down to a required background level. This test method can also be used for the segregation of soil lots by established contamination levels during on-site construction and excavation.

6. Interferences

6.1 The following elements typically are found in an X-ray spectrum from soil in the spectral region of uranium and thorium: zinc (Zn), tungsten (W), lead (Pb), rubidium (Rb), strontium (Sr), and yttrium (Y).

6.2 Rubidium is the primary interference for uranium, overlapping the uranium L-alpha-1 peak, and lead is the primary interference for thorium, overlapping the thorium L-alpha-1 peak. At typical levels for these elements all of the peak interferences can be eliminated by using a Gaussian mathematical peak fitting and deconvolution software routine. (Such is usually part of EDXRF instrumental software.) However, if the lead level is high (greater than 500 µg per gram), due, for instance, to the contamination of the soil by lead paint, then the peak segregation can become impossible. (A complete discussion of interelement effects and the correction models used to compensate for these effects is outside the scope of this procedure.) Explanations are found in several sources **(1, 2)**.[9]

6.3 Escape peaks (see 3.2.1) can interfere with the integration of the uranium and thorium L-alpha peaks and are therefore removed from the spectrum with a software operation (as is available with most instruments).

7. Apparatus

7.1 *Energy Dispersive X-Ray Fluorescence (EDXRF) System*, refer to Guide C 982.

7.1.1 *Photon Excitation Source*, capable of producing monochromatic X-rays of an appropriate energy to efficiently excite uranium and thorium, that is, from 2.72 E-15 to 3.52 E-15 Joules [J] (from 17 to 22 keV). Refer to Section 8 of Guide C 982. Either of the following sources is acceptable:

7.1.1.1 *Radioactive Source*, 109-Cd is well suited for efficient excitation. It should have an activity between 2.59 E + 08 and 3.70 E + 08 becquerels (between 7 and 10 millicurie).

7.1.1.2 *X-Ray Generator*, with high voltage power supply, rhodium target X-ray tube and a secondary target; molybdenum (Mo), rhodium (Rh) or silver (Ag) are suitable secondary targets.

7.1.2 *Solid State Detector [Si(Li)]*, with preamplifier maintained at liquid nitrogen temperature and capable of 2.64 E-17 J (165 eV) FWHM resolution or better using an Fe-55 radioisotope source with 1000 cps intensity of the emitted Mn K-alpha peak at 9.453 E-16 J (5.900 keV).

7.1.3 *Signal Processing and Data Acquisition Electronics*, includes: a bias power supply; a shaping amplifier or pulse processor using a 7.5 µs pulse shaping time constant; a pulse pileup rejector; an analog-to-digital converter (ADC); and multi-channel scaler.

NOTE 1—Automatic correction for count rate losses due to pulse pileup or electronics deadtime is achieved in the pulse processing electronics (as is available in most commercial X-ray units). Along with the automatic count rate correction, the maximum efficiency of the data acquisition system (that is, the preamplifier, pulse processor, and ADC) is achieved at a 50 % deadtime count rate. This is based on an electronic analysis of counting losses by the manufacturer. The X-ray tube current is therefore adjusted for a given sample matrix and set of excitation conditions to achieve a 50 % deadtime.

7.2 *Drying Oven*, controlled at 110 ± 5° Celsius.

7.3 *Analytical Jaw Tooth Crusher*, or equivalent, capable of crushing to 0.1 mm particle size.

7.4 *Laboratory Vacuum Cleaner*, with a high efficiency particulate air (HEPA) filter element.

7.5 *Shaker/Tumbler*, capable of blending a large volume of dry soil (at least 100 g) in a sample container. The shaker/tumbler may have a capacity to blend several containers.

7.6 *Impact Grinding/Mixing Mill*, capable of accepting the vial in 8.2.3. An equivalent process may be used to achieve the particle size specified in the sample preparation Section 11.

[9] The boldface numbers in parentheses refer to a list of references at the end of the text.

7.7 *Hydraulic Press*, 2.22 E + 05 N (25 ton-force) load capacity.

7.8 *Desiccator*.

8. Reagents and Materials

8.1 *Reagents*—None.

8.2 *Materials*:

8.2.1 *Evaporating Dishes*, glazed porcelain, size No. 7 or larger, with a 2.00 E-4 m^3 (200 mL) capacity.

8.2.2 *Watch Glasses*, size appropriate to cover the evaporating dish.

8.2.3 *Grinding/Mixing Vial Set*, with two mixing balls, made of steel or tungsten carbide, ball diameters of nominally 13 mm (0.5 in.), with a grinding sample capacity of 10 cm^3. An equivalent process and set of materials may be used to achieve the same particle size specified in the sample preparation section.

8.2.4 *Die Press Set*, 31 mm diameter with a maximum load capacity in excess of 2.22 E + 05 N (25 ton-force).

8.2.5 *Retaining Cup*, aluminum, 32 mm diameter, suitable for the die press.

9. Hazards

9.1 Refer to NBS Radiation Safety Handbook Number 111 and the Hazard Section of Guide C 982 for the hazards associated with the use of X-ray equipment.

9.2 When cleaning out the grinder and sample mixing vials with course sand or crushed glass, the resultant finely powdered glass is a health hazard if inhaled; crystalline silica can cause silicosis if exposure occurs on a regular basis. All such operations must be performed in a properly functioning exhaust hood.

10. Sampling, Test Specimens, and Test Units

10.1 Practice C 998 gives a practice for sampling of surface soil to obtain a representative sample for analysis of radionuclides. Guide D 420 provides a guide for investigating and sampling soil and rock materials at subsurface levels but is mainly concerned with geological characterization. The method described in Test Method D 1587 may be used to sample the soil using a thin-walled tube. If the soil is too hard for pushing, the tube may be driven or Practice D 3550 may be used. The method described in Test Method D 1586 may also be used to sample the soil and includes discussion on drilling procedures and collecting samples which are representative of the area. In the case of sampling rocky terrain, diamond core drilling may be used (see Practice D 2113). Where disturbed sampling techniques can be afforded, Practice D 1452 can be used, that is, using an Auger boring technique. The size of the sample is based on achieving a representative sample. Tube samples can be composited to achieve such a sample. Refer to the standards mentioned above that discuss obtaining a representative sample.

11. Sample Preparation

11.1 As stated in the scope, the analysis is performed on a dry weight basis, however, the percent moisture of the soil sample can be determined during the following steps by measuring the weight before and after drying. This provides the opportunity to calculate and report the data on an as-received basis or the percent moisture can be reported separately. Transfer the laboratory soil sample into an evaporating dish and cover the dish with a watch glass. Place the evaporating dish into a drying oven maintained at 105° Celsius. Allow it to dry for a minimum of 18 h. Remove the dish from the oven and allow it to cool to room temperature.

NOTE 2—It is recommended that a sample preparation log be developed and implemented by the user which details and tracks the steps of preparation for each sample. For each sample, the sample preparation log would list: the jaw tooth crusher; mixing vial number; grinder/mixing mill; and die press set used, as well as the preparer's name, and the date and time of preparation. Such a log is useful in backtracking cross contamination or sample carry over problems that are detected from the blank, standard, and control sample data (see 13.2). When multiple pieces of equipment are used for any one of the processing steps, the equipment should be numbered and the vials and die sets should be scribed with numbers for tracking purposes.

11.2 A Geiger-Muller counter may be used to survey the dried soil as a means of segregating any with a high level of contamination. High activity level samples can then be prepared on a separate jaw tooth crusher, if available, and the cleaning process can be done twice to ensure against cross contamination.

NOTE 3—The count rate used to denote a high level sample will depend on the model of instrument used and its counting efficiency.

11.3 Adjust the particle size setting on the jaw tooth crusher to 0.1 mm.

NOTE 4—It is recommended that all crushing, tumbling, and mixing be performed in a properly functioning laboratory hood. Follow the vendor's instructions on the use of the jaw tooth crusher, shaker/tumbler, and the impact grinding/mixing mill devices. An equivalent process to the one described below using the jaw tooth crusher may be used to homogenize the soil and grind it to a particle size of U.S. Sieve 150 mesh with an aperture of 106 µm.

11.4 Prior to the initial use and after each consecutive use of the jaw tooth crusher, clean it out by running about 150 g of course sand through it. Then use a laboratory HEPA vacuum cleaner to vacuum out all residual sand from the collection tray, sample insertion region, etc.

11.5 Remove each sample from the evaporating dish and run it through the jaw tooth crusher, cleaning as directed above after each use. Collect the sample in a sample container suitable for tumbling, such as an 8 oz jar or disposable polyethylene container. The container must be less than three-fourths full to allow for adequate mixing in the tumbling process.

11.6 Place the sample on a shaker/tumbler for an appropriate amount of time to allow for complete mixing. Consult the manufacturer's instructions to establish an appropriate mixing time.

11.7 Place approximately 15 cm^3 of sample into a mixing vial with two mixing balls and place the vial inside the grinding/mixing mill. Grind the sample for approximately 1500 s (25 min). An appropriate amount of time can be established from a series of test samples **(3, 4)** taken from a single homogenous sample with concentrations near the mid-range. The test samples would be prepared at incrementally longer grinding times and then analyzed. The appropriate

grinding time would be at the point in which any further increase in grinding time does not result in an appreciable increase in X-ray peak intensity.

11.8 The mixing vials are cleaned out after each use as follows:

11.8.1 Disassemble and rinse the vial components with water.

11.8.2 Blow or air dry the components and then reassemble the vial.

11.8.3 Place course ground glass or sand in the vial and run it on the grinding/mixing mill.

11.8.4 Remove the glass from the vial and wipe or blow out under a hood, the residual glass powder.

11.9 Place the finely powdered sample, or a portion of it, into the die press with an aluminum retaining cap. The cap helps to support the sample when pressed.

NOTE 5—The amount of sample placed into the die press is not critical for use in an EDXRF instrument in which the sample is inverted facing a lower mounted X-ray tube and detector, as long as the pellet is sufficiently thick to completely absorb the X-ray penetration.

11.10 Place the die press on the hydraulic press at a force of 2.22 E + 05 N (25 ton-force) for a minimum of 60 s. Then remove the pressed sample from the die. Mark the sample inside diameter (ID) on the back of the aluminum cap and handle the samples carefully so as not to abrade or disturb the surface.

11.11 Wipe out any remaining powder residue from the die with a wetted paper towel.

12. Preparation of Apparatus

12.1 The X-ray spectrometer must be allowed to reach the level of stability as specified by the manufacturer's instructions.

12.2 The detector supply of liquid nitrogen must be maintained.

12.3 Typical operating conditions are given in Table 1.

13. Calibration and Standardization

13.1 *Apparatus*:

13.1.1 *Peak Energy Calibration*—Calibrate the gain and offset on the pulse processor to ensure proper peak position according to manufacturer's instructions.

TABLE 1 Energy Dispersive X-Ray Fluorescence (EDXRF) Spectrometer Operating Conditions

For use of an X-ray Generator Excitation Source:	
X-ray tube anode target	Rhodium
Anode voltage (kV)	32
Anode current (mA)[A]	2.8
Secondary target	Molybdenum
Filter and thickness (mm)	Ag-(0.050)
For Use of a Radioisotopic Excitation Source:	
Radioisotope	Cadmium-109
Activity	2.59 E + 08 and 3.70 E + 08 becquerels
General Conditions:	
Atmosphere	vacuum (<70 Pa)
Counting live time (seconds)	1000
Energy range (keV)	0 to 20
Time constant (µseconds)	7.5
Detector columnator	Silver

[A]The anode current will vary between instruments. It should be set according to the manufacturer's instructions to achieve maximum efficiency of the data acquisition system (that is, the preamplifier, pulse processor, and ADC).

13.1.2 *X-Ray Energy Flux Monitoring*—Before a calibration is determined a factor, called the flux monitor ratio (FMR), is established to adjust for changes in the X-ray tube output or the X-ray energy flux. Refer to the terminology section for the definition of a flux monitor value and the flux monitor ratio. This factor can also be used to adjust for the rate of decay if a radioisotope source is used. The flux monitor ratio is the ratio of the initial flux monitor value (FMi) and the current flux monitor value at the time of sample analysis (FMc). Changes in the X-ray energy flux may occur as the tube ages and may change drastically shortly before the tube is to expire. Perform the following steps to establish the values: FMi, FMc, and FMR.

13.1.2.1 Select a metallic XRF standard (0.031 m in diameter) that can be analyzed under the same conditions as the samples (except for the change in the current to achieve maximum efficiency of the amplifier) giving a major peak or set of peaks in the same spectral region as the uranium and thorium, for example lead (Pb).

NOTE 6—The electrical current applied to the X-ray tube will be different between the metallic XRF standard and the samples since the electrical current must be adjusted to achieve a 50 % deadtime count rate, that is, a maximum efficiency of the data acquisition system. See Note 1. A metallic type standard is used because it can be preserved indefinitely and has good homogeneity and surface integrity.

13.1.2.2 Establish and set up operating conditions for the instrument to excite the major element or elements of the FM standard. These conditions should use the same secondary target as used for the samples in order to monitor the integrity of the secondary target surface at the same time. Likewise if a radioisotope source is used for the sample analysis, the same source should be used to monitor its radioactive decay as well as surface integrity.

13.1.2.3 Define a spectral region of integration along with sufficient acquire time to give a high number of counts (greater than 100 000 total accumulated counts) under the established set of conditions. A high number of counts is required for good precision and is representative of the X-ray energy flux.

NOTE 7—The spectral region of integration may include several peaks from one or more elements. The edges of the spectral region must be in the background of the spectrum to reduce the variation of the FMR value due to spectral shift. The exact same spectral region must be used for the determination of the initial flux monitor value (FMi) and the flux monitor value determined at the time of sample analysis (FMc) to reduce error in the FMR value.

13.1.2.4 Acquire a spectrum on the standard and integrate the spectral region defined above. This value, determined at the time of initial calibration, is set as the initial flux monitor value (FMi). This value, determined at the time of sample analysis, is FMc.

13.1.2.5 The flux monitor ratio (FMR) value is initially 1.0 at the time of calibration. At the time of sample analysis, repeat 13.1.2.2 and 13.1.2.3 to determine the value FMc. The FMR value is then calculated as follows:

$$FMR = \frac{FMi}{FMc} \tag{1}$$

13.1.3 *Instrument Operating Conditions*—Establish and set

up the operating conditions for the instrument in use with a current setting established for the soil matrix to achieve a 50 % deadtime count rate. Typical conditions are shown in Table 1. The conditions are kept constant for the calibration and the analysis of unknown samples.

13.2 *Reference Standards and Blanks*:

13.2.1 Use certified reference standards if found to be available. Other standards used for calibration and reference checks are made up to more completely cover the range of calibration using blank soil and solutions of uranium and thorium in nitric acid. Form a slurry by mixing the soil and solutions in about a 1:1 volume ratio. Then ground and dry the slurry in the same manner as the samples (see 11.1-11.6). Verify the concentrations by another validated method of analysis, such as colorimetry, fluorimetry, phosphorescence, etc. This same process can be used to generate matrix spiked quality control samples during a sample batch analysis.

NOTE 8—The dry mixing of elemental oxides with blank soil results in errors because of the segregation of oxide and soil particles due to particle size (and probably density) differences. Therefore, the dry mixing of oxide based standards is not recommended.

13.2.2 Obtain blank soil from locations offsite or away from any known source of radiological contamination at the surface level and on unfertilized soils. Analyze blank soil samples by another validated method of analysis to determine if the uranium and thorium concentrations are below the minimum detection limits of the EDXRF spectrometry technique prior to use as a blank.

13.2.3 Prepare reference standards and blanks in the same manner as samples. Maintain records of the preparation process on a sample preparation log (see Note 2). Enter blanks as well as duplicates and matrix spiked quality control (QC) samples if desired, into the sample preparation process from the initial point of drying the samples (see 11.1). The blank sample analysis is used to detect any problems with sample cross contamination during the preparation process. It is not used in the processing of spectra. Referring back to the sample preparation log, along with the other results from a series of samples may indicate where contamination has occurred, particularly where a high level sample has preceded the blank in the use of one of the preparation devices. This can indicate the need to improve or modify the cleaning process. Also as a means of checking, a second portion of the dried and ground blank can be reanalyzed and if the result equally exceeds the minimum detection limit then this would point to the jaw tooth crusher as the source of contamination.

13.2.4 Enter reference standards and blind controls into the sample preparation process at the point of using the grinding/mixing mill (see 11.7). This is after the standards have been dried, ground, and analyzed by another validated method of analysis to verify the concentrations. Refer to Test Methods D 4697 and E 882 for the establishment of quality control charts and a guideline of what to do in case the analysis of a standard is out of control. Standards that are found to be out of control can be the result of cross contamination, as similarly described for blanks. The sample preparation log should also be referred to in these circumstances to aid in determining the source of the problem.

13.3 *Calibration Curves and Tables*:

13.3.1 Using reference standards ranging in concentration of uranium and thorium from 20 to 1000 µg/g prepare and run them under the instrument operating conditions established in 13.1.3.

13.3.2 Process the sample spectra to remove the escape peaks and the background. Then integrate the peaks to obtain the intensities of the uranium and thorium L-alpha-1 peaks while taking into account peak overlap and interferences. The uranium and thorium L-alpha-1 peak energies are at 2.086 E-15 J (12.966 keV) and 2.190 E-15 J (13.613 keV), respectively.

13.3.3 Prepare separate calibration curves of concentration versus the L-alpha-1 peak intensity for uranium and thorium. Perform a linear least-squares calibration of the data of the form:

$$C = A \times I + B \tag{2}$$

where:

C = concentration (in µg/g),
I = intensity (in counts per second),
A = slope of curve, and
B = Y-axis intercept.

This may be part of the instrumental software package. The equation to be used in the calculation of unknown samples includes the FMR value as follows:

$$C = A \times I \times (FMR) + B \tag{3}$$

The minimum detection limit can be estimated by adding two times the calculated standard deviation of the Y-intercept to the Y-intercept value. For a more accurate determination of the detection limit refer to Practice E 876 and to the referenced articles by Hubaux and Vos **(5)** and Neter, Wasserman and Kutner **(6)**.

13.3.4 The calibration is found to be linear over the specified range without the use of interelement corrections or correction for varying concentrations of light element material. However these corrections can be adopted for both the calibration and sample analysis if they are provided in instrumentation software.

13.3.5 The linear coefficient of correlation can be used to determine the quality of the calibration of the instrument. Refer to 7.3.3 in Practice E 305. Generally for the concentration range indicated for uranium and thorium, the coefficient of correlation is greater than 0.95.

14. Procedure

14.1 Acquire and process the FM standard spectra and calculate the FMR value as directed in 13.1.2 and in accordance with any manufacturer's recommendations. It is recommended that data be tabulated to determine statistically when the FMR value represents a significant change or drift in the X-ray energy flux and to judge how frequently it is necessary to measure the FMR value.

14.2 Acquire the sample data under the conditions determined appropriate in 13.1.3 and as used for the calibration. The conditions must be the same for the unknown samples as the conditions used for the standards. Reference standards, blanks, and blind controls must also be prepared and analyzed by the

same procedure as the unknown samples. Run one blank and one reference standard for every ten samples.

14.3 Process the sample spectra to remove the escape peaks and the background. Then integrate the peaks to obtain the intensities of the uranium and thorium L-alpha-1 peaks while taking into account peak overlap and interferences.

15. Calculation

15.1 Using the linear calibration curve determined in 13.3 along with the FMR value, determine the concentrations of uranium and thorium based on the intensity values.

15.2 *Example*—The calculated equation for U is $C = 5.027 \times I \times (\text{FMR}) + 9.62$ and the calculated equation for Th is $C = 5.691 \times I \times (\text{FMR}) + 14.92$, where C = concentration in units of ppm and I = intensity in units of counts/second. The measured intensities for U and Th are 5.17 and 12.58 counts/second respectively. The FMR is 1.0. For U: $C = 5.027 \times 5.17 + 9.62 = 35.6$ micrograms per gram. For Th: $C = 5.691 \times 12.58 + 14.92 = 86.5$ micrograms per gram.

16. Precision and Bias

16.1 *Precision*—The precision of the instrumental analysis is shown in Table 2. The same pressed pellet of standard NRM 4 was analyzed 19 times over a period of twelve weeks. During this time no change was made in the flux monitor ratio (FMR) value. The precision of the analysis, without taking into account the error associated with the FMR value or the sample preparation, is indicated in Table 2 by the absolute and relative standard deviations for the uranium and thorium. The relative standard deviation of the FMR value alone, determined from 28 different determinations, is 0.024. Use of a computer generated instrument method for subtracting the background keeps the background removal consistent and improves the precision of the instrumental analysis. The combined precision of the sample preparation and the instrumental analysis is also shown in Table 2 for the reference standard R890417-051. This sample was reprepared and analyzed twelve times over a period of 20 weeks. During this time period the FMR value was determined weekly and did not vary outside of one standard deviation. The relative standard deviations for both uranium and thorium are similar to standard NRM 4. Thus there is no measurable loss of precision if the method of sample preparation is followed carefully. In Table 3 the certified reference standards were prepared and analyzed nine times within a one week period. Here the precision is essentially the same for the different standards and slightly improved compared to standard R890417-051.

16.2 *Bias*:

16.2.1 A uniform bias or systematic error between both the uranium and thorium concentrations can be indicative of a change in the X-ray energy flux; that is, the need to recalculate the FMR value. Variation in sample density or moisture content is not considered a significant cause of bias when the sample preparation technique described is used. A bias of one on the constituents can be the result of a peak interference of an element not accounted for in the peak integration and deconvolution process.

16.2.2 The analyses of the certified reference standards in Table 3 indicate that no bias is present in this test method. All of the results are within one standard deviation of the certified concentrations.

16.2.3 If suitable certified standards of uranium and thorium in soil are not available for instrument calibration and one must rely on determinations from another method of analysis, that is, colorimetry, it is possible that a bias can be transferred from the other method. If certified standards are used that do not originate from one's own geographic area, a bias can result from the possible differing matrix composition.

TABLE 2 Certified Reference Standard Data for U and Th in Soil[A]

NOTE 1—Units of (µg/g).

NOTE 2—The analyses shown were performed over a period of 20 weeks, each on a separate day. During this time no change was made in the flux monitor ratio (FMR) value. The certified concentration for standard NRM 4 is 35.6 µg U/g and 86.5 µg Th/g. The concentration for standard R890417-051 certified by colorimetric analysis is 182 µg U/g and 73 µg Th/g.

Repeat Analyses on the Same Pressed Pellet of Standard, NRM 4		Repeat Preparations and Analyses of Standard R 890417-051	
U	Th	U	Th
36	84	177	78
37	84	176	77
35	85	190	77
36	88	179	80
38	87	183	79
36	86	172	76
39	97	172	76
36	84	170	73
37	85	171	78
39	86	171	74
36	84	173	77
36	80	177	79
37	85		
37	83		
35	85		
35	83		
37	81		
37	82		
37	84		

U for Standard NRM 4		Th for Standard NRM 4	
Mean value	36.63	Mean value	84.89
Sample standard deviation	1.16	Sample standard deviation	3.51
Relative standard deviation	0.03	Relative standard deviation	0.04
U for Standard R890417-051		Th for Standard R890417-051	
Mean value	175.92	Mean value	77.00
Sample standard deviation	5.90	Sample standard deviation	2.04
Relative standard deviation	0.03	Relative standard deviation	0.03

[A]This standard was certified by supplier: UNC Geotech, contract operator of the DOE Technical Measurements Center, Grand Junction, Colorado.

17. Keywords

17.1 energy dispersive X-ray fluorescence (EDXRF); soil; thorium; uranium

TABLE 3 Certified Reference Standard Data for U and Th in Soil[A]

NOTE 1—Units of (µg/g).

NRM 4		NRM 5		NRM 6	
U	Th	U	Th	U	Th
36.3	88.0	68.3	164.2	130.2	314.7
36.4	85.0	67.6	160.7	132.6	316.6
36.3	87.2	67.4	164.6	130.8	315.6
35.0	84.5	64.0	160.1	129.6	318.6
36.9	86.3	67.1	164.1	129.0	312.9
35.4	86.9	66.4	165.2	125.6	312.6
37.1	87.0	64.7	162.0	126.5	305.6
35.0	85.1	67.8	168.1	126.0	312.9
36.0	89.9	68.2	164.0	126.0	310.7
Certified Concentrations± Standard Deviations					
35.6 ± 3.3	86.5 ± 5.5	67.5 ± 4.8	163.9± 10.0	128.2 ± 10.2	313.3 ± 10.0
Mean Values					
36.04	86.65	66.83	163.6	128.4	313.3
Sample Standard Deviation					
0.766	1.686	1.528	2.443	2.533	3.759
Relative Sample Standard Deviation					
0.021	0.019	0.022	0.014	0.019	0.011

[A]These standards were certified by supplier: UNC Geotech, contract operator of the DOE Technical Measurements Center, Grand Junction, Colorado.

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